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TRANSLATION
ORGANIC SILICON COMPOUNDS
(KREMNIYORGANICHESKIYE SOEDINENIYA)

By K. A. Andrianov
State Scientific Technical Publishing House for Chemical Literature Moscow, 1955

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TRANSLATION

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This book is a monograph on the chemistry of organo-
silicon compounds and is intended for scientists, engineering
and technical personnel of plant laboratories, instructors,
post-graduate students, and students of higher educational
institutions.

This book contains information on the methods of
preparation, physical and chemical properties of a large
number of monomeric organosilicon compounds, as well as the
methods of preparation, properties and applications of high-polymer
organosilicon compounds.

TO THE READER

The publishing house requests you to send your remarks and
comments on this book to the address Moscow, K-12 Novaya
ploshchad', 10, pod'yezd 11, Goskhimizdat

Kuz'ma Andrianovich Andrianov

ORGANOSILICON COMPOUNDS

Editor M.V.Sobolenskiy

Technical Editor Ye.G.Shpak

Delivered to type setters 22 April 1955. Proofs approved for printing
12 December 1955

Paper 70 x 108 1/16 = 16.25 sheets = 44.5 quires

Accounting number
of sheets 46.5

Edition 4000 copies

Price 25.25 Rubles

Order No. 640

Printing Plant of Goskhimizdat, Moscow, 88 Ugreshskaya

F-TS-9191/V
The past few decades have been marked by major advances in the development of the monomeric organosilicon compounds. Considerable results have been achieved both in the study of the monomeric compounds and in the development of methods of preparing and studying the structure and properties of high-molecular organosilicon polymers. Many new and interesting facts have been established, which have deepened our knowledge in this field of chemistry and allow us to draw a number of theoretical and practical conclusions. These conclusions enable us to approach more deeply the development of the synthesis of the monomeric, and in particular, of the polymeric organosilicon compounds, and to modify their properties in the desired direction.

The advances in the synthesis of organosilicon compounds, and the valuable properties of the polymere products prepared and the materials produced from them have led to the rapid development of their production, and their utilization in many sectors of the national economy. Organosilicon compounds have found widespread use in the manufacture of heat-resistant high-grade electric insulating materials, in insulating varnishes, in the production of electric generators and other electrical devices, transformers and other electrotechnical equipment. The use of organosilicon compounds in electrical technology permits a sharp increase in the reliability of operation of machines and equipment, a reduction in their weight, and saving in the consumption of materials, and opens up possibilities for the creation of new and more improved electrical machines, apparatus, etc. A large number of
organosilicon polymers are of great value as heat-resistant and anti-corrosive coatings for metals, allowing operations at temperatures from 360°C to 500°C, for the manufacture of aerofoil and heat resistant plastics and laminated dielectrics, and also in the production of precision castings not requiring machining.

Liquid silicon polymers are used in the manufacture of various lubricants, hydraulic and damper liquids, employed over a wide range of temperatures above and below freezing. Fillers based on organo-silicon elastomers allow operation of units at a temperature up to 250°C and higher.

The high hydrophobic properties of organo-silicon compounds are used to make glass, paper, wool fabrics, ceramics, bedding materials, etc. unwettable.

The field of application of organosilicon compounds is continuously expanding. But the large amount of experimental materials, both on the synthesis and on the study of the properties of various products, that has been accumulated up to now, as scattered among the pages of numerous literature sources, mainly scientific journals, and in his work the research chemist often loses much time on finding the information he needs. For this reason we have made an attempt, in this monograph, to systematize, and, in a number of cases, also to discuss critically, the literature on hand on the chemistry of organosilicon compounds from its very beginning up to about the middle of 1954, and to present it, starting out from the basic ideas which have been built up in the author's mind as a result of many years of work in this field. I recognize that a number of fundamental questions in the chemistry of organosilicon compounds cannot be fully answered in this book, there are often contradictions between various reported data, and it will require a large amount of experimental and theoretical work to eliminate these contradictions and give a consistent interpretation of the reported facts. This book does not consider the methods of analysis of organosilicon compounds, since the reader will find such material in the book by Professor A.P.Kreshkov and his associates* (for footnote, see next page). I have likewise not considered the properties and methods of pre-
paring various materials based on organosilicon polymers in combination with asbestos, mica, glass wool, glass fiber, etc., since I am preparing a separate book on this subject for the press.

In the exposition of the material I have held to the classification and nomenclature of organo-silicon monomers and polymers published in collaboration with A.V. Topchiyev in Izv. AN SSR (1953).

I express my profound gratitude to S.A. Golubtsov, who participated in the compilation of Chapters IV and VI, and to M.V. Sobolevskiy, who was of great assistance to me in editing the book.

I shall be grateful for all comments made by readers of the book.

K. Andrianov

---

INTRODUCTION

BRIEF REVIEW OF THE DEVELOPMENT OF THE CHEMISTRY OF THE ORGANOSILICON COMPOUNDS

The study of the chemistry of silicon compounds commenced in 1825, when silicon tetrachloride was synthesized. The discovery of organosilicon compounds dates back to 1845, when esters of silicic acid were prepared from silicon tetrachloride and alcohol. The experimental studies covering the period from the 1820's to 1890's (works of Wohler and Buff; Ladenburg; Friedel and Crafts, and others) led to the synthesis of various inorganic and organic silicon compounds. Among the inorganic compounds, SiH₄, SiHCl₃, SiHBr₃, SiHI₃, etc. were prepared during this period; while the organic silicon compounds included tetra-substituted silanes, alkyl- and aryl-chlorosilanes, esters, and substituted esters of orthosilicic acid.

The similarity in structure and in certain properties between organic compounds and the organic compounds of silicon led to the idea of the complete similarity between the compounds of silicon and carbon. This view lasted until D.I. Mendelyev demonstrated that between the properties of carbon and silicon compounds there exist not only similarities but also substantial differences. In comparing the silicon compounds known at that time with the carbon compounds, he pointed out the slight resistance for instance of compounds between silicon and hydrogen and halogens to the action of water, which sharply distinguishes them from the analogous carbon compounds. Thereby he put an end to the incorrect, one-sided approach to the chemistry of organosilicon compounds (Bibl.1).
Mendeleyev was the first to establish that the compounds of silicon with oxygen, unlike the compounds of carbon with oxygen, have a polymeric structure.

The second period began in the 1890's and continued to the 1930's. It is difficult to draw a sharp line between these two periods, but for this period in the development of the chemistry of organosilicon compounds, the influence of the proposition established by Mendeleyev, that there are differences between silicon and carbon compounds, is characteristic.

In the 1890's, Stokes (Bibl.2) was the first foreign scientist to recognize that certain compounds of silicon, for example \((\text{SiOCl}_2)_x\) are high-molecular polysiloxanes. He stated that he had reached the conclusion that this compound had a polymeric structure as a result of studying the work of Mendeleyev (referring to the Second German Edition of "Principles of Chemistry"). These views were then developed in the works of Stokes and his associates, and of other authors. During this period the school of Kipping and other investigators (Bibl.3) synthesized a large number of compounds and considerably improved the research technique. It was found that the fundamental difference between silicon and carbon resides in the fact that carbon is able to combine with equal ease with electronegative and electropositive elements, while the silicon atom has a greater tendency to combine with electronegative elements and groups.

The beginning of the third period in the development of the chemistry of organosilicon compounds may be placed in the 1930's, that is, at the time when the first studies in the field of the synthesis and study of the high-molecular organosilicon compounds appeared.

As far back as Mendeleyev (Bibl.1), who was the first to pose scientifically the question of the structure of silica and its hydrates, the cause of the difference between the properties of carbon dioxide and silicon dioxide was considered to reside in the polymeric character of silicon dioxide.

Butlerov (Bibl.4) pointed out that silicic, phosphoric and tungstic acids and
their inorganic derivatives form hydroxyl-containing compounds of complex composition, which are then dehydrated to full or partial anhydrides. The studies of Soviet chemists from 1935 to 1939 (Bibl.5) established that organosilicon compounds containing oxygen, like SiO₂ or other organic oxygen-containing silicon compounds have an exceptional tendency to form polymers. Polymers containing siloxane groups and side organic radicals directly bound to the silicon atoms were first synthesized and described in these works, and received the name of organosiloxanes.

These works (Bibl.5) laid the foundation for the development of the chemistry of the high-molecular organosilicon compounds of the type of the polyorganosiloxane; they showed the possibility of applying the polyorganosiloxanes in the most varied fields of technology. The wide use of the polyorganosiloxanes in turn led to a large field of research, not only in the synthesis of new polymers and the study of their properties, but also in the synthesis of new organosilicons as the starting materials for polymers. In this connection a large number of papers devoted to monomeric and polymeric organosiliconos, often containing contradictory data, appeared in periodicals.

The present author has set himself the task of critically examining and systematizing the extensive material accumulated in the literature on the synthesis and investigation of an extremely important type of polymers, the polyorganosiloxanes, as well as the intermediates for their synthesis, the halo-derivatives of silicon, the esters and substituted esters of orthosilicic acid, the alkylchlorosilanes and arylchlorosilanes, etc. with the object of facilitating their use by both scientific and plant workers.

**Silicon and its Properties**

Silicon, next to oxygen, is the most widespread element (by weight). The earth's crust, according to geochemical calculations (based on the works of V.I. Vernadskiy, A.Ye.Fersman, and others), is composed of about 27% of silicon (Bibl.6). While carbon is the most important element in the composition of plant and animal
organisms, silicon is the principal element in the composition of substances of mineral origin. Silicon compounds are also contained in hair, wool, and feathers; in the stalks of certain plants, the grasses, the horse-tail weeds, etc., in the shells of many infusoria, in the bodies of sponges, etc.

Silicon was isolated in the free state in 1811 by Gay-Lussac and Tenard by passing the vapor of silicon fluoride over metallic potassium, but they did not describe it as an element.

In 1823, Berzelius gave a description of the silicon isolated by him from potassium fluosilicate by treating it with metallic potassium at a high temperature.

\[ K_2SiF_6 + 4K \rightarrow 6KF + Si \]

In its purest state, elementary silicon may be prepared by the action of magnesium on pure silica by the reaction:

\[ 2Mg + SiO_2 \rightarrow 2MgO + Si \]

It is industrially prepared in large quantities by reducing silicon with carbon in electric furnaces.

\[ SiO_2 + 2C = Si + 2CO \]

Silicon occupies the position in the fourth group of the Mendeleyev periodic system immediately below carbon, of which it is an analog. This was why organosilicon compounds were at first regarded as simple analogs of organic compounds. It was subsequently found, however, that the organosilicon compounds have a number of peculiarities characteristic of them alone, and therefore form an independent field of chemistry.

Silicon, like carbon, may either give up or take up electrons, but its ability to take up electrons, and consequently, its metalloidal properties, are somewhat less pronounced than those of carbon. This fact is of great importance not only for
the difference in the chemical reactions of these two elements, but also for the properties of their compounds.

It is interesting to compare certain properties of silicon and carbon, and to consider the hydrolytic and thermal stability of the bonds of these elements in various compounds with other elements.

The atomic weight of silicon is 28.09. Three isotopes of mass 28, 29, and 30 are known. It is insoluble in water. In the finely dispersed state it is hygroscopic and gives off adsorbed water only at red heat. Crystalline silicon conducts electricity, its hardness on the metallurgical scale is between 6 and 7, and its specific gravity is 2.34–2.49. Amorphous silicon has the specific gravity* 2.00–2.35. The melting point of silicon is 1420°C. Its linear expansion coefficient (Bibl.7) $a_{40} = 0.00000763$.

The atomic weight of carbon is 12.001, that of its isotope is 13. It is non-hygroscopic, and forms two crystalline forms, diamond and graphite, and an amorphous form, coal. Carbon is infusible and nonvolatile; it is converted into the vapor state at 3000°C. Graphite and coal possess electrical conductivity; the diamond is a typical dielectric. When either diamond or coal are heated above 1000°C, they are gradually converted into the most stable form, graphite.

Elementary silicon enters into combination with hydrogen at the temperature of the electric arc, forming silicon hydride (SiH₄) (Bibl.8). Silicon reacts with

*The dimensionless quantity formerly called the "specific gravity" (ratio of the weight of a body to the weight of an equal volume of water at temperature $t^\circ$) is customarily called the relative weight in modern terminology.

The relation between the weight of a body and its volume is called the specific gravity and is expressed in g/cm$^3$. Since most of the information given in this book has been taken from literature sources, the old terminology will be retained here and hereafter.
nitrogen at 1000°C to form silicon nitride, SiN; carbon also forms C2N2 in very small quantities, but only at 1800°C.

Fluorine and other halogens react more readily with silicon than with carbon. Fluorine combines with silicon at room temperature, chlorine at 200-300°C, bromine at 500°C, and iodine at a still higher temperature. Carbon in the form of coal likewise reacts with fluorine at room temperature.

Carbon does not react with chlorine, bromine nor iodine.

Silicon oxidizes with relative difficulty in air, but readily in oxygen. Carbon, in the form of porous coal, begins to oxidize in air at a temperature under 100°C, graphite at about 650°C, diamond at over 800°C. Acids do not act on carbon nor silicon. Only hydrofluoric acid acts on silicon. Water, in the presence of alkalies (which evidently play the role of catalysts) reacts with silicon, giving off hydrogen. The reaction takes place in two stages:

\[\text{Si} + 3\text{H}_2\text{O} \rightarrow \text{H}_2\text{SiO}_3 + 2\text{H}_2\]
\[\text{H}_2\text{SiO}_3 + 2\text{KOH} \rightarrow \text{K}_2\text{SiO}_3 + 2\text{H}_2\text{O}\]

Carbon does not react with water under ordinary conditions.

At a high temperature, the oxides of silicon and carbon form silicides and carbides:

\[\text{SiO}_2 + 4\text{Mg} \rightarrow \text{Mg}_2\text{Si} + 2\text{MgO}\]
\[\text{CaO} + \text{C} \rightarrow \text{CaC}_2 + \text{CO}\]

The atoms of carbon are easily bound with each other, forming open or closed carbon chains. The number of atoms making up such chains may be very large. Molecules composed of a few hundred and even a few thousand atoms of carbon linked with each other are entirely stable. In this respect silicon differs sharply from carbon. Silicon atoms form bonds with each other only with difficulty, and such bonds are not very strong, as a result of which the number of atoms in molecules contain-
ing the bonds -Si-Si-Si- is very limited, and at the present time does not exceed 14.

Carbon and silicon form strong bonds with many elements. The strength of a bond is usually determined by the thermochemical method. Table 1 gives data characterizing the strength of the bonds of carbon and silicon with certain elements (Bibl.9).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Energy kcal/mol</th>
<th>Interatomic Distance A</th>
<th>Bond</th>
<th>Bond Energy kcal/mol</th>
<th>Interatomic Distance A</th>
</tr>
</thead>
<tbody>
<tr>
<td>C—C</td>
<td>62.77</td>
<td>1.54</td>
<td>Si—C</td>
<td>58</td>
<td>1.93 ± 0.03</td>
</tr>
<tr>
<td>C—H</td>
<td>85.56</td>
<td>1.14</td>
<td>Si—H</td>
<td>75</td>
<td>1.54</td>
</tr>
<tr>
<td>C—Cl</td>
<td>70</td>
<td>1.69—1.77</td>
<td>Si—Cl</td>
<td>85</td>
<td>2.00</td>
</tr>
<tr>
<td>C—Br</td>
<td>57</td>
<td>1.94</td>
<td>Si—Br</td>
<td>69</td>
<td>2.14</td>
</tr>
<tr>
<td>C—I</td>
<td>43</td>
<td>2.10</td>
<td>Si—J</td>
<td>51</td>
<td>2.43</td>
</tr>
<tr>
<td>C—F</td>
<td>104</td>
<td>1.35—1.42</td>
<td>Si—F</td>
<td>143</td>
<td>1.54</td>
</tr>
<tr>
<td>C—O**</td>
<td>75</td>
<td>1.43</td>
<td>Si—O**</td>
<td>88</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Si—Si</td>
<td>12.5</td>
<td>1.90 ± 0.03</td>
</tr>
</tbody>
</table>

*This Table gives data for the corresponding symmetrical compounds, for instance Si(CH\textsubscript{3})\textsubscript{4}, SiCl\textsubscript{4}, etc.

**For the siloxane bond.

The compounds of carbon and silicon differ sharply in their resistance to hydrolysis. Thus, while compounds of carbon with hydrogen, halogens, nitrogen, and sulfur, at ordinary temperatures, are not hydrolyzed by water in the presence of acids and bases, compounds of silicon with these elements are very easily hydrolyzed under the same conditions.

THE STABILITY OF THE BOND BETWEEN SILICON AND OTHER ELEMENTS

The Silicon—Carbon Bond

Compounds containing the bond —Si—C— occupy a position intermediate between
organic and organometallic compounds. The organosilicon compounds are very diverse, and the available experimental material on their behavior on heating and under the action of chemical reagents is still insufficient to establish general regularities characterizing the bond \(-\text{Si-O}\) -.

The addition of an organic radical to silicon, that is, the formation of the bond \(-\text{Si-O}\) -, takes place in various ways, and depends on the nature of the starting substances and the reaction conditions.

When certain silicon compounds react with organic substances, the formation of the bond \(-\text{Si-O}\) - is hindered, and requires severe conditions; other compounds form the same bond under very mild conditions. This may be illustrated by the following examples. The heating of silicon tetrachloride for several months at 150°C with such alkylating agents as \((\text{CH}_3)_2\text{Al}\), \((\text{CH}_3)_2\text{Hg}\) or \((\text{CH}_3)_2\text{Zn}\), does not lead to the formation of organosilicon compounds (Bibl.10). With the chlorosilanes \(\text{H}_2\text{SiCl}_3\) and \(\text{H}_2\text{SiCl}_2\), however, these reactions take place under mild conditions. Diphenylmercury forms organosilicon compounds with \(\text{SiCl}_4\) only when heated in a sealed vessel to 300°C (Bibl.11).

The difficulty of the formation of new \(-\text{Si-O}\) - bonds increases with the number of organic radicals bound to the silicon atom (especially with aromatic radicals.

Attempts to prepare tetraarylsilanes by the action of arylorganomagnesium compounds on chlorosilanes were long unsuccessful, and this method was considered unsuitable for this purpose (Bibl.12). However, by raising the temperature to 140°C, it was finally possible to effect the replacement of all halogen atoms in halosilanes (Bibl.13) by aromatic radicals.

Under these conditions it was possible to obtain completely substituted organic
derivatives of even the higher silanes, starting out from such halogen derivatives as
$\text{Si}_2\text{Cl}_6$, $\text{Si}_2\text{Br}_6$, $\text{Si}_3\text{Cl}_8$, or from the oxychlorides and oxybromides of silicon,
$\text{Si}_2\text{OCl}_6$, $\text{Si}_2\text{OBr}_6$, $\text{Si}_3\text{O}_2\text{Br}_8$, etc. (Bibl.14).

The halogen atoms attached to the silicon atom also exert an influence on the
formation of organosilicon compounds from halosilanes. Thus, in the series $\text{SiF}_4$,
$\text{SiCl}_4$, $\text{SiBr}_4$, the energy of the bond $-\text{Si}-X$ decreases sharply from 143 kcal for the
bond $-\text{Si}-\text{F}$ to 69 kcal for the bond $-\text{Si}-\text{Br}$. For this reason the possibility of form-
ing the bond $-\text{Si}-\text{C}$- in a reaction becomes progressively easier from fluosilicate to
bromosilicate (Bibl.15).

Bond $-\text{Si}-\text{C}$- in organosilicon compounds is almost purely covalent; its energy of
formation is close to the energy of formation of the $-\text{C}-\text{C}$- bond. Studies of tetra-
methylsilane, hexamethyldisilane, trimethylchlorosilane, and dimethyldichlorosilane,
and of cyclic organosiloxanes have shown that in the first two of these compounds,
the interatomic distances $-\text{Si}-\text{C}$- correspond, within the limits of experimental
error, to the calculated sum of the covalent radii of the Si and C atoms*.

In the methylchlorosilanes, this distance decreases as the number of chlorine
atoms attached to the silicon atom increases (Bibl.16). We give below the inter-
atomic distances $-\text{Si}-\text{C}$- in methylsilanes and methylchlorosilanes.

*The sum of the covalent radii of the Si and C atoms equals
$1.17 + 0.771 = 1.941\ \text{Å}$
The thermal stability of the -Si-C- bond is determined by the type and size of the organic radical and of the other atoms or groups bound to the silicon atoms. The tetra-substituted silanes have exceptionally high thermal stability; thus, according to certain data, tetramethylsilane begins to decompose only at 650-700°C (Bibl.17). These temperatures are very high, and their authenticity appears very doubtful. As we have succeeded in establishing, for polydimethylsiloxanes, the CH₃-Si- bond begins to break down at 300-350°C.

Dolgov's studies have shown that in the tetra-substituted silanes, the stability of the -Si-C- bond to heating in an atmosphere of hydrogen increases on transition from aliphatic to aryl-substituted compounds. These studies showed that, as a result of the long heating of tetraethylsilane and hexamethyldisilane at 350-360°C, they decompose, with cleavage of 50% of the ethyl radicals, forming ethane. Under the same conditions, 15% of triethylphenylsilane decomposes while tetraphenylsilane remains unchanged, even at 450°C (Bibl.18).

The chemical stability of the -Si-C- bond depends on the structure of the organic radical bound to the silicon atom, the molecular structure of the organosilicon compound as a whole, and on the nature of the reagent involved. Under the action of concentrated sulfuric acid on methylpentylpropylbenzylsilane, only the methyl radical is cleaved, and when it acts on tetra-substituted alkylarylsilanes,
the aryl radical is cleaved, while the alkyl radical is cleaved with greater difficulty (Bibl.19).

The action of fuming sulfuric acid on aliphatic substituted esters of orthosilicic under mild conditions does not lead to rupture of the \(-\text{Si-C-}\) bond, but its action on mixed alkyl-(aryl)-substituted esters under the same conditions lead to cleavage of the phenyl group. Chlorosulfonic acid cleaves the isobutyl radical from methylisobutylbenzylsilane, but in dibenzylpropylethylsilane it does not cleave the organic radical, but merely sulfonates the benzyl groups (Bibl.20).

Fuming HCl on prolonged heating at 90° C with an alkylphenylsilane cleaves the phenyl radical. Dialkyl- and diaryldichlorosilane, as well as trialkyl- and triaryl-chlorosilanes, are less sensitive to the action of fuming HCl; the bond \(-\text{Si-C-}\) in them is not ruptured even on heating with HCl at 200° C (Bibl.21).

Under the action of nitric acid on phenyltriethylsilane, diphenyldiethylsilane, triphenylethylsilane, and tetraphenylsilane, the bond \(-\text{Si-C-}\) is not broken, but the aromatic nuclei are nitrated instead.

The action of chemical reagents on the aminophenylsilanes is interesting. Under the action of acid and alkalies on \(p\)-aminophenylsilanes, they are decomposed, with rupture of the \(-\text{Si-C-}\) bond, and formation of aniline and hydroxysilanes, while the \(m\)-aminophenylsilanes are not decomposed on boiling with HCl nor with alkali solutions. The aminophenylsilanes are likewise brominated and acetylated without breaking the \(-\text{Si-C-}\) bond (Bibl.22).

When bromine acts on tetraarylsilanes at high temperatures, there may be not only bromination of the aromatic nuclei but also rupture of the \(-\text{Si-C-}\) bond. This
is observed, for instance, when bromine acts on tetraphenylsilane:

\[(\text{C}_6\text{H}_5)_4\text{Si} + \text{Br}_2 \rightarrow (\text{C}_6\text{H}_5)_3\text{SiBr} + \text{C}_6\text{H}_4\text{Br}\]

Under the action of halogens on aliphatic tetra-substituted silanes, the organic groups are not cleaved (Bibl. 23).

The bond between silicon and carbon is relatively stable to the action of alkalies. They are able to break it only under very severe conditions. Thus, for example, the methyl groups in hexamethyldisiloxane, in polydimethylsiloxanes, and in polymethylsiloxanes are cleaved only on treatment of the compounds with aqueous alkalies in an autoclave under pressure, and at temperatures of 200°C or over (Bibl. 25). In this case methane and sodium silicate are formed. The cyclic tri- and tetraorganosiloxanes undergo similar cleavage. Ladenburg has shown that the organohydroxy silanes cleave the organic radical when boiled with alkali (Bibl. 24).

Concentrated alkalies at high temperatures, in the presence of solvents containing hydroxyl, decompose hexamethyldisiloxane, liberating methane, while in the presence of solvents not containing hydroxyl, the siloxane bonds themselves are ruptured.

The introduction of a halogen atom into aliphatic radicals bound to a silicon atom sharply modifies the properties of the \(-\text{Si-C-}\) bond (Bibl. 26).

The influence of the position of the halogen atom (with respect to the silicon atom) in the organic radical on the strength of the \(-\text{Si-C-}\) bond under the action of various chemical reagents has been studied in a number of works. It has been established that chloromethyltrichlorosilanes with chloromethyl group containing less than three atoms of chlorine resist hydrolysis at the \(-\text{Si-C-}\) bonds by an acid catalyst, but are cleaved by an alkali, or by KCN or Na CN solutions. Hydrolysis
becomes easier with increasing degree of chlorination of the methyl group. Thus, the trichloromethyltrichlorosilanes are easily hydrolyzed by water according to the following formula:

\[ \text{CH}_3\text{SiCl}_3 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 3\text{HCl} + \text{HCl}_2 \]

This reaction has been used to establish the structure of various chloromethyl-chlorosilanes. Thus, for example, when methyldi(chloromethyl)chlorosilane,

\[ \text{CH}_2\text{Cl} \text{Si-Cl} \text{CH}_2\text{Cl} \], is treated with hot alkali, methyl chloride is formed, but when hot alkali acts on dimethyldichloromethylchlorosilane, \( \text{(CH}_3\text{)}_2\text{Si} \text{-Cl} \text{CHCl}_2 \text{-Cl} \), methylene chloride is formed instead.

\( \alpha \)-chloroethyltrimethylsilane, \( \text{(CH}_3\text{)}_2\text{SiCHClCH}_2 \), according to Ushakov and Itenberg (Bibl.27), is decomposed only with great difficulty by alcoholic alkali; thus, trimethylvinylsilane is formed only after 9 hours heating at 145° in a sealed tube.

\( \beta \)-chloroethyltrimethylsilane, \( \text{(CH}_3\text{)}_2\text{SiCH}2\text{CH}_2\text{Cl} \), is easily hydrolyzed by 1.5 N aqueous alkali (Bibl.28).

The reaction of cleavage of the halogen atom bound to the \( \beta \)-carbon atom was accompanied by rupture of the -Si-C- bond regardless of the nature of the chemical reagent used for cleavage of the halogen. The only difference observed was in the velocity of rupture of the -Si-C- bond. The reaction proceeded according to the formula:

\[ \text{ClCH}_2 \text{-CH}_2\text{-Si} \text{(C}_3\text{H}_4)_2 + 2\text{H}_2\text{O} \rightarrow (\text{C}_3\text{H}_4)_2\text{Si(OH)}_2 + 2\text{HCl} + \text{C}_4\text{H}_4 \]

The reaction of \( \beta \)-chloroethylidistyethylchlorosilane, \( \beta \)-chloroethylidistyethylfluoro-
silane, and \( \beta \)-chlooroethyltriethylsilane with the following substances was investigated: alcoholic alkalies, aqueous alkalies, potassium acetate in acetic acid, methylmagnesium bromide, aluminum chloride, silver nitrate in alcoholic solution (Bibl.29). The ethylene liberated during the reaction was absorbed by bromine.

Table 2 gives data on the results of this study.

Table 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reagents</th>
<th>Temperature, ( \degree C )</th>
<th>Yield of Ethylene in ( % ) of Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Water</td>
<td>20</td>
<td>30-40</td>
</tr>
<tr>
<td>2, 3</td>
<td>Water</td>
<td>20</td>
<td>( \leq 1 )</td>
</tr>
<tr>
<td>2</td>
<td>Water</td>
<td>100</td>
<td>35-45</td>
</tr>
<tr>
<td>1, 2</td>
<td>1.25 N NaOH</td>
<td>20</td>
<td>85-90</td>
</tr>
<tr>
<td>3</td>
<td>The Same</td>
<td>20</td>
<td>( \leq 55 )</td>
</tr>
<tr>
<td>3</td>
<td>50% CH(_2)OH</td>
<td>100</td>
<td>( \leq 5 )</td>
</tr>
<tr>
<td>3</td>
<td>1.25 N in 50% CH(_2)OH</td>
<td>100</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>1, 2, 3</td>
<td>CH(_3)OH</td>
<td>100</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>1</td>
<td>1.25 N KOH in CH(_3)OH</td>
<td>20</td>
<td>70-75</td>
</tr>
<tr>
<td>2</td>
<td>The Same</td>
<td>20</td>
<td>60-70</td>
</tr>
<tr>
<td>1</td>
<td>1.25 N CH(_3)ONa in CH(_3)OH</td>
<td>20</td>
<td>60-70</td>
</tr>
<tr>
<td>2</td>
<td>The Same</td>
<td>20</td>
<td>60-70</td>
</tr>
<tr>
<td>3</td>
<td>The Same</td>
<td>20</td>
<td>&lt; 10</td>
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<tr>
<td>Compound</td>
<td>Reagents</td>
<td>Temperature, °C</td>
<td>Yield of Ethylene in % of Theoretical</td>
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</tr>
<tr>
<td>1, 2</td>
<td>Glacial CH₃COOH</td>
<td>100</td>
<td>&lt;10</td>
</tr>
<tr>
<td>1, 2</td>
<td>1.25 N CH₃COOK in CH₃COOH</td>
<td>100</td>
<td>30-50</td>
</tr>
<tr>
<td>1, 2</td>
<td>Dry Pyridine</td>
<td>100</td>
<td>&lt;5</td>
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<td>1, 3</td>
<td>0.2 N AgNO₃ in CH₃OH</td>
<td>20</td>
<td>95-97</td>
</tr>
<tr>
<td>2</td>
<td>The Same</td>
<td>20</td>
<td>45</td>
</tr>
</tbody>
</table>

Experiments have shown that nucleophilic reagents easily rupture the Si-C bond in β-chloroethylidethylfluorosilane and β-chloroethylidethylchlorosilane.

β-chloroethyltriethylsilane is considerably more stable, and it reacts, with the breaking of the Si-O-bond, only under the action of a 1.25 NaOH solution and of a 0.2 N solution of silver nitrate in methanol.

The Si-C bond in organosilicon compounds containing a halogen atom bound to the γ-carbon atom is destroyed by hydrolysis. In this case, cyclopropane may be formed (Bibl.30):

\[
\begin{align*}
&\text{CH}_3 \\
&\text{CH}_3 \begin{array}{c} \downarrow \text{Si} \\uparrow \text{Cl} \\
&\text{CH}_3 \text{CH}_2 \text{CH}_2 \text{Cl} \\
&\text{CH}_3 \\
\end{array} + \text{CH}_3 \begin{array}{c} \downarrow \text{Si} \\uparrow \text{Cl} \\
&\text{CH}_3 \text{CH}_2 \text{CH}_2 \text{Br} \\
&\text{CH}_3 \\
\end{array} + \text{CH}_2 \\
&\text{CH}_3 \downarrow \\
\end{align*}
\]

The reaction depends to a considerable degree on the reagent and on the conditions of cleavage of the product.

γ-bromopropyltrimethylsilane (CH₃)₂SiCH₂CH₂Br (I) and γ-chloropropyltrimethylchlorosilane Cl₂SiCH₂CH₂Cl (II) were investigated.

γ-bromopropyltrimethylsilane (product I) in the presence of AlCl₃ (1% of the weight of product I) is decomposed with the liberation of cyclopropane (92% of theoretical). The reaction is initiated spontaneously in the cold. The mixture is then heated to 70°C. The residue in the flask consists of trimethylbromosilane.
When product I is boiled 5 hours with an excess of a 20% solution of KOH and 50% ethanol, cyclopropane is not liberated, but the halogen is completely split off. When γ-chloropropyltrichlorosilane (product II) reacts with a 30% solution of KOH in absolute ethanol, cyclopropane (31%) is liberated. The reaction begins at room temperature, but for completion it requires addition of aqueous alkali and heating of the mixture to boiling.

Under the action of AlCl₃ on II, cyclopropane is not liberated. The reaction product has a higher boiling point than the initial product, and consists of a mixture of uninvestigated substance.

The mechanism of the formation of cyclopropane on the hydrolysis of organosilicon compounds containing halogens bound to the γ-carbon atom depends on the reagent; thus, on hydrolysis by water, the nucleophilic agent (hydroxyl) attacks the silicon atom:

\[
\text{H-O} + \text{Si-CH₃-CH₂-CH₂-X} \rightleftharpoons \text{HO-Si-CH₃-CH₂-CH₂...X} \rightarrow \text{HO-Si-CH₂-C₃H₇} + X^-
\]

The replacement of the halogen atoms by methyl groups leads to a lowering of the electrophilic activity of the silicon atom, and the cleavage reaction does not take place. Under the action of aluminum chloride, which is a more powerful electrophilic agent than silicon, ionisation takes place at the C-X bond, and the complex [AlX₄] is formed:

\[
\text{Si-CH₃-CH₂-CH₂-X + AlX₄} \rightarrow \text{Si-CH₂-C₃H₇} + [AlX₄]^- \rightarrow \text{Si-X + H₂C-CH₃ + AlX₃}
\]

The presence of a triple bond in the radical attached to the silicon, as shown...
by Vol'nov and Reutt in their study of phenylvinyltrialkoxy silanes, so strongly reduces the strength of the -Si-C- bond that the action of water is enough to rupture it (Bibl.31). In this case the following reaction occurs:

$$C_6H_5C ≡ C ≡ CH(OC_2H_5)_3 + 2H_2O \rightarrow 3C_6H_5OH + C_6H_5C ≡ CH + SiO_2$$

On treatment of compounds containing the allyl radical, \( CH_2 = CH - CH - CH_2 Si(OC_2H_5)_3 \) with water, dilute acids or dilute alkalies, no cleavage of the organic radical was observed (Bibl.32).

In silicon compounds containing the vinyl radical, for instance \( CH_2 = CH - Si - (OR)_3 \), the -Si-C- bond is likewise not destroyed by water, dilute acids nor dilute alkalies.

As will be seen from these examples, the stability of the Si-C bond is affected by the presence of triple bonds or a halogen in the organic radical, and by their position with respect to the silicon atom, but the introduction, for instance, of halogens into the aromatic radical does not weaken the Si-C bond. Thus the experimental material available on this subject is still inadequate for establishing definite regularities characterizing the influence of the composition and structure of the substituent on the strength of the -Si-C- bond.

Dichlorophenyltrichlorosilane and trichlorophenyltrichlorosilane are substances of exceptional chemical stability; the -Si-C- bond in them and in the polymers based on them cannot be broken by the action of dilute alkali, sulfuric or nitric acid.

The resistance of the -Si-C- bond in organosilicon compound to the action of...
oxygen has not been studied sufficiently. The available observations relate mainly to the action of oxygen on polymeric organosilicon compounds containing both \(-\text{Si}-\text{C}\-\) and \(-\text{Si}-\text{O}-\text{Si}\-) bonds in the same molecule. Polymeric organosilicon compounds (polyorganosiloxanes) have higher resistance to the action of heat and oxygen than purely organic compounds containing the \(-\text{C}-\text{C}\-) bond, although, as shown above, the values for the bond energy of \(-\text{Si}-\text{C}\-\) and \(-\text{C}-\text{C}\-) are close together. Thus, for example, the aliphatic hydrocarbons (paraffin) on heating in a current of air, begin to oxidize, with rupture of the \(-\text{C}-\text{C}\-) bonds, at temperatures somewhat higher than 100°C. The polymeric organic compounds, polystyrene, polyethylene, polyisobutylene, etc., have a high sensitivity to the action of oxygen at temperatures over 100°C. This is confirmed by the fact that they age under the conditions of practical use in industry at temperatures over 120°C. The polyorganosiloxanes, as is commonly known, begin to oxidize only at 180-200°C. In this connection it is important to explain the causes of the higher stability of organosilicon polymeric compounds containing \(-\text{Si}-\text{C}\-) bonds.

On rupture of the \(-\text{Si}-\text{C}\-) bonds, the products of the oxidation of the organic radicals are aldehydes, acids, etc. These oxidative processes may be represented schematically as follows (Bibl.33):
The explanation for the thermal stability of the polyorganosiloxanes must be sought in the difference between the oxidation products of silicon and carbon. It is well known that silicon, in contrast to carbon, does not yield gaseous oxidation products, but, on oxidation, forms polymeric substances of the type \((\text{Si}_2\text{O})_n\). The thermal stability of polymeric organosilicon substances under the action of oxygen is due to the exceptional stability of the siloxane bond in the main chain of the molecule, and to the appearance of an additional siloxane bond in the place formerly occupied by an organic radical that has been oxidized. In this case an increase in total molecular weight is observed, in contrast to the behavior of organic polymers, which, on oxidation, as a result of the breaking of the carbon chain, form volatile products, with a decrease in the total molecular weight of the polymer. This circumstance, in our opinion, is what determines the exceptional stability of polymeric organosilicon compounds (polyorganosiloxane) by comparison with organic compounds.

The thermal and oxidative processes affecting the \(-\text{Si}-\text{C}-\) bond lead only to a rearrangement, but not the destruction of the chain of polyorganosiloxanes, while thermal degradation and oxidative processes in organic polymers are accompanied by rupture of the \(-\text{C}-\text{C}-\) bond in the molecular chains and the side groups, with the formation of gaseous products.

The liberation of volatile products, formed owing to the oxidation of the fragments of the molecular chains and side groups in organic polymers, encourages the increased access of oxygen to the still intact chains of the molecules, and, as a rule, these processes take place at an ever increasing velocity. In polyorganosiloxanes, under the same conditions, what happens is, for the most part, rupture of the \(-\text{Si}-\text{C}-\) bond, accompanied by cleavage of the organic radicals in the form of oxidation products (aldehydes, acids, etc.). The chains themselves are not destroy-
ed in this case. The detachment of the organic radicals is accompanied by the formation of oxygen bridges between the chains of the polyorganosiloxane molecules, limiting the access of oxygen to the unaffected organic radicals, as a result of which further oxidation is retarded. The detachment of organic radicals on heating and the action of oxygen takes place more easily in polyorganosiloxanes containing aliphatic radicals. The polyorganosiloxanes containing aromatic radicals or mixed aromatic-aliphatic radicals are oxidized with greater difficulty by oxygen, owing to the greater stability toward oxidation of the phenyl radical, and to the formation, during the oxidation process, of antioxidants (phenols) which reduce the effectiveness of the action of oxygen on the \(-\text{Si-C}\) bond.

The possibility of the existence of a multiple bond \(-\text{Si=C}\) is disputed at the present time, in spite of Schlenk's statement that he had prepared the compound \((\text{C}_6\text{H}_5)_2\text{Si=CH}_2\). In later studies, products of this type were not obtained. In those cases where one might expect the formation of compounds with the multiple bond \(-\text{Si=C}\) (the reaction of methylene chloride with a silicon-copper alloy), the cyclical compound \((\text{Cl}_2\text{SiCH}_2)_n\) or the open-chain compound \(\text{Cl}_3\text{SiCH}_2\text{SiCl}_3\) was obtained; on the reaction between dichlorethane and an alloy or mixture of silicon and copper, hexachloroethylenedisilane, \(\text{Cl}_3\text{SiCH}_2\text{CH}_2\text{SiCl}_3\), was obtained.

Certain reactions connected with the cleavage of an organic radical are regarded as a stepwise process, in which the siliconium ion (Bibl.35), which is said to be formed as an intermediate product, plays a great role. This explanation of the mechanism of the reaction has been advanced without direct proof and is based mainly on the fact that silicon, as an element of more electropositive character than carbon, should form a positive siliconium ion more readily than carbon forms the carbonium ion.

From this point of view, the hydrolysis of \(\beta\)-oxypropyltrimethylsilane should be
represented as follows:

\[
\begin{align*}
\text{OH} & \quad \text{HOH} \\
(\text{CH}_3)_3\text{Si}-\text{CH}-\text{CH}_3 + \text{H}^+ & \rightleftharpoons (\text{CH}_3)_3\text{Si}-\text{CH}-\text{CH}_3 \\
& \rightleftharpoons (\text{CH}_3)_3\text{Si}-\text{CH}-\text{CH}_3 + \text{H}_2\text{O} \\
& \rightleftharpoons (\text{CH}_3)_3\text{Si} + \text{CH}=\text{CH}_3 + \text{H}_2\text{O} \\
& \rightleftharpoons (\text{CH}_3)_3\text{SiOH} + \text{CH}=\text{CH}_3 + \text{H}^+ \\
\end{align*}
\]

The formation of -onium compounds is accelerated when the acidity of the medium is increased or when electron-donor groups are introduced into the aromatic radical. For example, for triphenylfluoromethane, for which the formation of carbonium ions has been demonstrated, the introduction of methyl groups into the aromatic nucleus in the para-position accelerates the process of hydrolysis:

Hydrolysis is slowed with increasing pH.

The opposite relationship has been established for triphenylfluorosilane. The introduction of methyl groups into the aromatic nucleus in the para position retards hydrolysis by a factor of about 5, while, on increase of the pH, there is a sharp acceleration (by \(10^6\) times) of hydrolysis. Thus the experimental data lead to doubt with respect to the possibility of formation of siliconium ions during the process of hydrolysis. It is more probable that the intermediate products in hydrolysis are compounds of penta-covalent silicon, of the type

\[
\begin{align*}
\text{C}_6\text{H}_5 \\
\uparrow + \begin{array}{c} \text{O-Si} \end{array} \\
\uparrow \begin{array}{c} \text{C}_6\text{H}_5 \text{C}_6\text{H}_5 \end{array}
\end{align*}
\]
which then cleave according to the reaction:

\[ \text{H}_2\text{OSi(C}_6\text{H}_5)_3\text{F}^+ \rightarrow \text{H}_2\text{OSi(C}_6\text{H}_5)_3^+ + \text{F}^- \rightarrow \text{HO-Si(C}_6\text{H}_5)_3 + \text{H}^+ + \text{F}^- \]

Such a mechanism is in complete agreement with the experimental data, and explains why hydrolysis is accelerated in an acid medium.

The Silicon-Oxygen Bond (Siloxane Bond)

Most known organosilicon polymers are constructed of siloxane chains...

... -O-Si-O-Si-O-Si-..., in which the silicon atoms are also bound to organic radicals. The thermal stability of the silicon-oxygen bond is very high. Quartz melts at about 1800°C, but heating it to temperatures below the melting point causes no perceptible destruction of the bonds -Si-O-Si-. In the organosilicon polymeric compounds (polyorganosiloxanes), the thermal stability of the siloxane bond is considerably lower than in quartz and the silicates, and depend on the number of organic radicals attached to the silicon atom. With increasing number of organic radicals attached to the silicon atom, the thermal stability of the siloxane bond decreases. The structure of the molecules of polyorganosiloxanes, (cyclic or linear) likewise exerts an influence on the thermal stability of the -Si-O-Si- bond.

A study of the thermal stability of polydimethylsiloxanes of the structure HO-[\((\text{CH}_3)_2\text{SiOl}_2]-\text{Si(\text{CH}_3)_2OH}\) shows that on heating them to 400°C, without access of air, they are decomposed with formation of low-molecular cyclic polymers \([\text{(CH}_3)_2\text{SiOl}]_n\), where \(n = 3, 4, 5, 6\) or more. On such thermal treatment, about 44% of the trimer, 24% of the tetramer, 9% of the pentamer, 10% of the hexamer, and about 16% of compounds more highly polymerized than the hexamer, are formed. It is characteristic that the content of methyl groups in the starting polymer and in the product obtained from it remained unchanged. The structure of the polymer is modified...
by the breaking of some siloxane bonds and the formation of new ones (Bibl.36).

Under the action of concentrated sulfuric acid, the reverse process of transformation of cyclical polymers into linear polymers is also possible. The polydiethylsiloxanes undergo such a rearrangement with greater difficulty than the polydimethylsiloxanes. The polymonomethylsiloxanes, polymonoethylsiloxanes, and polyphenylsiloxanes do not undergo such a rearrangement, with cleavage of the $-\text{Si-O-Si-}$ bond under the action of high temperatures and concentrated sulfuric acid.

The siloxane bonds in quartz are very stable to the action of chemical reagents, and are ruptured only under the action of hydrochloric acid and strong alkalies. Sulfuric, nitric, and other acids have no action on them.

The attachment of organic radicals to the silicon atom rarely modifies the chemical properties of the siloxane bonds.

Fluorine compounds are most energetic in destroying the siloxane bond in the polyorganosiloxanes. Under the action of ammonium fluoride in the presence of sulfuric acid on hexamethyldisiloxane, the $-\text{Si-O-Si-}$ bond is broken, and trimethylfluorosilane is formed. The reaction takes place under mild conditions.

Under the action of sulfuric acid on the polyorganosiloxane, the siloxane bond may be not only rearranged but also destroyed. If we act on hexamethyltrisiloxane with 20% oleum, then hexamethylenedisiloxane sulfate is formed by the reaction:

\[
(CH_3)_3SiO-Si(CH_3)_3 + H_2SO_4 \rightleftharpoons (CH_3)_2Si-O-SO_2-O-Si(CH_3)_3 + H_2O
\]

The siloxane bond may also be destroyed by the action of ammonium chloride in concentrated sulfuric acid on hexamethyldisiloxane (Bibl.28):

\[
2\text{NH}_4\text{Cl} + [(CH_3)_2Si]_3O + H_2SO_4 \rightleftharpoons 2(CH_3)_2SiCl + (\text{NH}_4)_2SO_4 + H_2O
\]

Diethylchlorosilane cannot be prepared by this method. When phosphorus tri-
bromide acts in the presence of ferric chloride on hexamethyldisiloxane, the
-\text{Si}-\text{O}-\text{Si}- bond is broken and trimethylchlorosilane is formed. When concentrated
sulfuric acid acts on cyclic polydimethylsiloxanes in the presence of disiloxanes or
without them, these cyclic compounds can be converted into linear ones. In this
case, the siloxane bond in the cyclic polymer is broken under the action of sulfuric
acid, according to the equation (Bibl.37):

\[
\left(\left(\text{CH}_3\right)_{3}\text{SiO}\right)_{x} + \left(\text{CH}_3\right)_{3}\text{SiO} \xrightarrow{\text{H}_2\text{SO}_4} \left(\text{CH}_3\right)_{3}\text{SiO}\left(\left(\text{CH}_3\right)_{3}\text{SiO}\right)_{x} - \text{Si}\left(\text{CH}_3\right)_3
\]

A study of equilibrium systems of cyclic and linear polymethylsiloxanes, es-
pecially after their treatment with sulfuric acid, shows the absence of cyclic
trimers (Bibl.38). This would argue for the presence of high stresses in the
six-membered ring built up of silicon and oxygen atoms. According to data of
Andrianov and Skipetrov, the valence angle -\text{Si}-\text{O}-\text{Si}- in polyethyilsiloxanes is 168°;
in polymethylsiloxanes, according to the determinations of Sauer and Mead, this
angle is 160 ± 15°. Consequently in the six-membered ring, in which the value of
the angles amounts to almost 109°28', greater stresses arise. In cyclic hydrocar-
bons the production of high stresses in the ring is possible, owing to the interfer-
ence of the substituent groups or atoms of hydrogen. In the case of polyorgano-
siloxane rings, the substituent groups are further apart, and there is practically
no interaction between them; the high sensitivity of cyclical polyorganosilicones
to the action of even small quantities of sulfuric acid is consequently explained by
the stress of the siloxane bond in them. The siloxane bond in linear polyalkyl-
siloxanes is considerably more resistant to the action of sulfuric acid.

The Silicon-Silicon Bond

In contrast to organic compounds, the organic and inorganic silicon compounds
containing the bond $\text{-Si-Si-}$ have a greater tendency to thermal decomposition and chemical transformations under the action of alkalies and oxygen. The inorganic halo-derivatives of di- and polysilanes begin to decompose when heated to a temperature a little over $200^\circ\text{C}$. When chlorosilanes are prepared by the action of chlorine on silicon at temperatures below $200^\circ\text{C}$, a large percentage of higher halo-silanes is obtained, but with increasing temperature, their proportion, due to thermal decomposition (Bibl.39), falls from 8.6% at 180-200$^\circ\text{C}$ to 4.0% at 300$^\circ\text{C}$. The low stability of the polysilanes should also explain the fact that no compounds with more than 14 silicon atoms in the molecule have been prepared.

Under the action of the oxygen of the air on the higher halosilanes, their oxidation takes place. The reaction takes place even in the cold with such energy that an explosion may occur. The higher chlorosilanes in this reaction pass over into chlorosiloxanes:

$$\text{Cl}_2\text{Si}-\text{Si-Cl}_2 + \text{O} \rightarrow \text{Cl}_2\text{Si-O-Si-Cl}_3$$

The fact that two electropositive silicon atoms are neighbors leads to the breaking of the bond, for instance in the case of the halo-derivatives of the higher silanes, even under the action of such alkylating agents as Grignard's reagent, or of $\text{HX} + \text{Na}$. In this case completely substituted monosilanes are formed (Bibl.40, 41).

In completely alkylated higher silanes, the $\text{-Si-Si-}$ bond is considerably more stable, and is not broken under the action of either sodium or halogens.

The great accumulation of phenyl groups in polysilanes leads to an increase in their stability. Thus, the polyphenylsilanes (for instance, tetrane) according to data of Kipping, are very stable (Bibl.42).
Kipping also states that dipropylidiphenylethyldisilane resists the action of an alkali solution. Usually, however, the polysilanes are decomposed quantitatively under the action of aqueous alkali. The reaction takes place with the liberation of hydrogen.

\[-\text{Si-Si-} + 2\text{H}_2\text{O} \rightarrow 2\text{Si-OH} + \text{H}_2\]

The qualitative decomposition of polysilanes at the -Si-Si- bonds under the action of moist piperidine takes place still more readily.

The elevated stability of the -Si-Si- bond in polyorganosilanes is probably due to steric hindrance. In this case, various organic radicals attached to the silicon atoms may have a different effect on the stability of the -Si-Si- bond. It is not very probable, however, that any combination of substituents could stabilize the molecular chains containing -Si-Si- bonds (Bibl.43) to such an extent as to make these compounds thermally and chemically as stable as the polyorganosiloxanes.

The Silicon-Halogen Bond

All silicon compounds, inorganic and organic alike, containing the -Si-X bond, have a pronounced halo-anhydride character, which becomes more intense as we pass from iodine to bromine, chlorine and fluorine. In contrast to carbon, silicon has an elevated power to form compounds with electronegative elements, and this is pronounced in its reactions with halogens. Many inorganic compounds, for instance
those like silicon tetrachloride and silicon tetrafluoride, are more than 70% ionized with respect to the \(-\text{Si-X}\) bond. For the halo-derivatives of silicon which also contain organic radicals in the molecule, we have still no data on the degree of ionization of the \(-\text{Si-X}\) bond. Silicon compounds with such bonds have an exceptionally high thermal stability, especially the tetrahalosilanes and arylhalosilanes. Thus, phenyltrichlorosilane withstands heating to over 400°C without decomposition; tetrachlorosilane even to over 600°C. Such alkylhalosilanes as dimethyldichlorosilane, ethyltrichlorosilane and diethylidichlorosilane, however, are less stable at elevated temperatures and are markedly dissociated at temperatures as low as about 300°C. The fluorides are an exception. According to the available data, they have a high stability at elevated temperatures. Thus, trimethylfluorosilane decomposes at 600°C. The characteristic difference between the \(-\text{Si-X}\) bond and the \(-\text{O-X}\) bond consists also in the fact that the halo-derivatives of silicon, of such series as \(\text{SiX}_4\), \(\text{HSiX}_3\), \(\text{H}_2\text{SiX}_2\), \(\text{H}_3\text{SiX}\), \(\text{HSi}X_3\), \(\text{R}_2\text{SiX}\) and \(\text{R}_3\text{SiX}\) (where \(\text{R}\) is an organic radical), do not react with magnesium (Bibl.44). Only the iodides dissolve magnesium and zinc; but the reaction with iodides have not yet been studied (Bibl.45). The resistance of the \(-\text{Si-X}\) bond to hydrolysis is exceptionally low, and in this respect this bond differs sharply from the \(-\text{O-X}\) bond. All the silicon compounds containing the \(-\text{Si-X}\) bond, whether inorganic or organic, react readily with water. In this case the \(-\text{Si-X}\) bond is hydrolysed and the \(-\text{Si-OH}\) bond is formed. The introduction of organic radicals into the molecule somewhat increases the hydrolytic stability of the \(-\text{Si-X}\) bond, but even in this case it still remains exceptionally sensitive to
water for the iodine, bromine, and chlorine derivatives. Even such compounds in which one atom of silicon is bound to two or three organic radicals are readily hydrolyzed quantitatively by cold water, regardless of the number and size of the organic radicals.

The number and size of the organic radicals have an influence only on the rate of hydrolysis. The rate of hydrolysis is slowed with increasing number of radicals bound to silicon, and with increasing size of the radical. This is particularly marked in the organofluorosilicon compounds. While the alkyl- and aryltrifluorosilanes are hydrolyzed instantaneously, the dialkyl- and diaryldifluorosilanes are hydrolyzed considerably more slowly by water.

The trialkyl- and triarylfuorosilanes are even more stable against hydrolysis; they can be distilled in air without appreciable decomposition, with no protection from moisture, and for their total hydrolysis they must be heated with alkali (Bibl. 46). The –Si–F bond in trialkylfluorosilanes has a lowered activity to the action of other chemical reagents as well; the fluorine in such compounds is not replaced by a radical by the aid of organomagnesium compounds.

Compounds with the –Si–X bond react easily with all compounds containing hydroxyl, forming esters. Trimethylchlorosilane reacts with strong sulfuric acid. In this case the –Si–Cl bond is broken, and hexamethyldisilane sulfate is formed:

\[2(\text{CH}_3)_3\text{SiCl} + \text{H}_2\text{Si}_4 \rightarrow 2\text{HCl} + (\text{CH}_3)_3\text{SiO}–\text{SO}_2–\text{OSi}(\text{CH}_3)_3\]

The Silicon-Nitrogen Bond

A large number of silicon compounds containing the Si–N bond are known, among them aminosilanes of type \(\text{Si}(\text{NH}_2)_4\), polyaminosiloxanes \(-\text{SiO}–\text{Si}–\), substituted

\[\begin{array}{ll}
\text{NH}_2 & \text{NH}_2 \\
\text{NH}_2 & \text{NH}_2 \\
\end{array}\]
aminosilanes of the type \( \text{Si(NHR)}_4 \), or poly-(organo)-aminosilanes \( \text{Si-\text{NH-Si-}} \), and so on.

They are all thermally stable compounds. All of them, however, are unstable to water and aqueous solutions, solutions of acids and alkalies, and the Si-N bond is broken in such reactions. The inorganic compounds of silicon and nitrogen withstand heating to high temperatures. Thus when metallic silicon is roasted in a stream of nitrogen at 1300°C, a mixture of the following silicon nitrides is formed: \( \text{Si}_3\text{N}_4 \), \( \text{Si}_2\text{N}_3 \), \( \text{SiN} \). Under the action of water, these compounds are decomposed, with liberation of ammonia and silicon dioxide:

\[
\text{Si}_3\text{N}_4 + 6\text{H}_2\text{O} \rightarrow 3\text{SiO}_2 + 4\text{NH}_3
\]

Alkalies also decompose silicon nitrides. The organosilicon nitrogen containing compounds are easily hydrolyzed by water, rupturing the -Si-N bond. The rate of hydrolysis depends on the size of the organic radical bound to the nitrogen.

Tetra-substituted compounds of the type \((\text{RN})_4\text{Si}\) are more readily hydrolyzed than poly-(organo)-aminosilanes.

Aminodisilanes can be obtained according to the reactions:

\[
2(\text{CH}_3)_2\text{SiCl} + 3\text{NH}_3 \rightarrow (\text{CH}_3)_3\text{SiNCH}_2\text{CH}_3 + 2\text{NH}_4\text{Cl}
\]

\[
(\text{CH}_3)_2\text{SiCl} + 2\text{NH}_2(\text{C}_2\text{H}_5)_2 \rightarrow (\text{CH}_3)_3\text{SiN}(\text{C}_2\text{H}_5)_2 + (\text{C}_2\text{H}_5)_2\text{NH-HCl}
\]

\[
(\text{CH}_3)_2\text{SiNHCH}_3 + (\text{CH}_3)_2\text{SiCl} \rightarrow [(\text{CH}_3)_3\text{Si}]_2\text{NCH}_3 + (\text{CH}_3)_3\text{SiNH-HCl}
\]

They are easily hydrolyzed in the presence of solvents.

The -Si-N bond in compounds of the type \((\text{CH}_3\text{O})_x\text{Si(NEt)}_4-x\) is more resistant to the action of water than in the aminodisilanes.
The Bond between Silicon and the Oxygen of the Ether Group

The ether bond $\text{Si-OR}$ in esters of orthosilicic acid $\text{Si(OR)}_4$, and especially in substituted esters of orthosilicic acids $R_x\text{Si(OR)}_{4-x}$, are slowly hydrolyzed by distilled water. This reaction is strongly accelerated in the presence of acids and alkalies.

The size and structure of the organic radical $R$, and the number of OR groups in the molecule, also affect the rate of hydrolysis of the esters and substituted esters of orthosilicic acid.

The esters of orthosilic acid are more readily hydrolyzed than the corresponding substituted esters of orthosilicic acid. An increase in the number of substitution groups $R'$ in the substituted esters of orthosilicic acid leads to a retardation of the hydrolysis reaction; thus alkyl- and aryltriethoxysilanes are hydrolyzed more readily than dialkyl- and diaryldiethoxysilanes, while the latter in turn are more easily hydrolyzed than trialkyl- and triarylethoxysilanes.

Diphenyldiphenoxsilane is very stable to the action of water and to a 5% alkali solution. Compounds whose organic radical contains a halogen are more sensitive to the action of water. Thus, tetra-$\beta$-chlorothoxysilane is more easily hydrolyzed than the ethyl ester of orthosilicic acid. Di-tert-butylidioethoxysilane is not hydrolyzed by water, owing to steric hindrance due to the presence of tertiary butyl groups in it.

The Silicon-Hydrogen Bond

The formation of a bond between silicon and electropositive elements close to it in the value of their electronegativity usually takes place with difficulty, while the products formed, such as, for instance, the silicon hydrides, are chemically unstable.

The silicon-hydrogen bond is not strong and is easily split not only by oxygen or halogens, but even by water in the presence of hydroxyl ions:
For the reaction to occur, the presence of the traces of alkali extracted from the glass apparatus is sufficient. The hydrogen of silane can be replaced by chlorine even under the action of HCl, with the formation of the corresponding halo-derivative.

INFLUENCE OF THE SILICON ATOM ON THE BEHAVIOR OF GROUPS AND ATOMS CONNECTED WITH IT THROUGH OTHER ATOMS

The silicon atom can increase or decrease the activity of organic functional groups linked with it through other atoms.

The silicon atom makes a chlorine atom attached to the β-carbon atom of an organosilicon compound susceptible to hydrolysis in the cold under the action of aqueous alkali. Thus, β-chloroethyltrichlorosilane reacts with an alkali in the following way:

$$\text{CICH}_2\text{CH}_2\text{SiCl}_3 + 4\text{NaOH} \rightarrow \text{C}_2\text{H}_6 + \text{Si(OH)}_4 + 4\text{NaCl}$$

The chlorine attached to the γ-carbon atom is quantitatively cleaved under the action of an alcoholic solution of KOH.

On treatment with alkali, compounds containing chlorine attached to the α-carbon atom do not cleave the chlorine. The reaction proceeds according to the formula:

$$\text{CH}_2\text{CHClSiCl}_3 + \text{NaOH} \rightarrow \text{CH}_3\text{CHClSi(OH)}_2 + 3\text{NaCl}$$

Thus, according to their capacity for cleavage of Cl atoms, the organosilicon compounds containing chlorine in the organic radical may be arranged in the following series:

$$\gamma > \beta > \alpha$$
On the chlorination of ethyltrichlorosilane, the chlorine goes mainly to the ϒ-position, in spite of the fact that the methylene group is usually more reactive than the methyl group. Apparently the hydrogen atom, like the halogen atoms, in an organosilicon compound, are more firmly bound to the α-carbon atom than to the ϒ-atom.

The silicon atom reduces the tendency of an adjacent multiple bond to participate in addition and polymerization reactions. Thus, Vol'nov and Reut (Bibl.32) found that an alkyvinyltrithoxysilane adds bromine incompletely at its triple bond.

It is well known that unsaturated alkylentrichlorosilanes are easily distilled without polymerization. The retarding influence of the silicon atom on polymerization becomes ineffective if two unsaturated groups add to a single silicon atom; thus, for example, dialkylenedichlorosilanes, in contrast to alkylentrichlorosilanes, do polymerize on distillation.

PRINCIPLES OF THE CLASSIFICATION AND NOMENCLATURE OF ORGANO SILICON COMPOUNDS

As the chemistry of organosilicon compounds developed, repeated attempts were made to formulate a rational classification and nomenclature of these compounds. Even today, however, there is still no single classification and nomenclature established and recognized by all.

Kipping in 1905 (Bibl.47), and Martin (Bibl.48) in 1913, proposed a nomenclature of organosilicon compounds, but it was not widely adopted. Stock (Bibl.49) in 1916 published a nomenclature that was more widely adopted. But the attempts in this direction still continued. In 1944 Sauer (Bibl.50) proposed a nomenclature of organosilicon compounds. Subsequently, the recommendations of an American committee to develop a rational nomenclature of these compounds were published (Bibl.51, 52).

In 1950, A.P.Kreshkov (Bibl.53) proposed a nomenclature which likewise has still not been widely adopted.

By organosilicon compounds we mean any compound of silicon containing carbon,
in contrast to the rule adopted in element-organic chemistry, where element-organic compounds are usually taken to mean only such compounds in which the carbon is necessarily attached to an atom of the element involved. In collaboration with A.V. Topchiyev, I attempted, taking into account the experience of both of us, to construct a classification and nomenclature of organosilicon compounds (Bibl.54, 55), and I shall adhere to it in the present book.

The classification of organosilicon compounds which I shall use is constructed on the basis of the following nomenclature. All organosilicon compounds are divided into two groups:

1. Low-molecular organosilicon compounds.
2. High-molecular organosilicon compounds.

Low-Molecular Organosilicon Compounds

The name of the low-molecular organosilicon compounds is based on the name of the first member of the series of the simplest compounds of one class or another. The silicon hydrides are taken as the starting substances in the classification, while all the remaining representative of this class are considered as their derivatives, that is, as compounds arising from the replacement of one, two, three, or four hydrogen atoms in such silicon hydrides by organic radicals, organic atom groups, or by other atoms.

The Silicon Hydrides (Silanes)

The silicon hydrides are the class of inorganic silicon compounds in whose molecule the silicon atoms are bound to each other and to hydrogen atoms. The general formula of the saturated silicon hydrides is \( \text{Si}_n \text{H}_{2n+2} \). The simplest representative of this class, \( \text{SiH}_4 \), is called silane, its homologs \( \text{H}_2 \text{Si-SiH}_3 \), disilane; \( \text{H}_3 \text{Si-SiH}_2 \text{SiH}_3 \), trisilane; \( \text{H}_4 \text{Si-SiH}_2 \text{SiH}_2 \text{SiH}_3 \), tetrasilane, and so on.

Thus the silicon hydrides form a homologous series in which each succeeding member differs from the preceding member by one \( \text{SiH}_2 \) group.
When one or more hydrogen atoms in the homologous series of silicon hydrides are replaced by radicals or organic groups, and the hydrogen is simultaneously replaced by functional groups (for instance, X-halogen), the corresponding homologous series of organosilicon compounds are formed.

The following may be, for example, such radicals and atomic groups:

<table>
<thead>
<tr>
<th>Radicals</th>
<th>Atomic Groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl CH$_3$-</td>
<td>Acetyl CH$_3$CO-</td>
</tr>
<tr>
<td>Ethyl C$_2$H$_5$-</td>
<td>Propionyl CH$_3$CH$_2$CO-</td>
</tr>
<tr>
<td>Vinyl CH$_2$ = CH-</td>
<td>Benzyol C$_6$H$_5$CO-</td>
</tr>
<tr>
<td>Ethynyl CHC.-</td>
<td>Methoxy CH$_3$O-</td>
</tr>
<tr>
<td>Phenyl C$_5$H$_6$-</td>
<td>Phenoxy C$_6$H$_5$O-</td>
</tr>
<tr>
<td>Chlorophenyl ClC$_6$H$_4$-</td>
<td>Acetamido CH$_3$CONH-</td>
</tr>
<tr>
<td>Naphthyl C$_{10}$H$_7$-</td>
<td>Anilino C$_6$H$_5$NH-</td>
</tr>
<tr>
<td>etc.</td>
<td>etc.</td>
</tr>
</tbody>
</table>

The present state of the study of organosilicon substances corresponds to their division into the following great classes:

**Substituted Silanes**

The compounds of this class are regarded as products of the substitution of one or several atoms of hydrogen in the simplest silicon hydride, SiH$_4$, by like or unlike radicals.

If the silicon atom is attached to one radical, then the compound is called a monosubstituted silane, if to two, three or four radicals, it is called a di-, tri-, or tetra-substituted silane respectively.

Substituted silanes with unlike radicals attached to the silicon atom are called mixed substituted silanes. The designation of the radicals is constructed according to the rational nomenclature adopted in organic chemistry. The names for the substituted silanes are made up of a number and the name of the radicals, followed by the termination "silane".
For instance:

\[
\begin{align*}
&\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-SiH}_3 \quad \text{butylsilane} \\
&\text{CH}_3\text{-CH}_2\text{-SiH}_3 \quad \text{tert-butylsilane} \\
&\text{CH}_3\text{-CH-CH}_2\text{-SiH}_3 \quad \text{isobutylsilane} \\
&\text{CH}_3\text{-SiH}_2 \quad \text{methylsilane} \\
&\text{ClCH}_2\text{SiH}_3 \quad \text{chloromethylsilane} \\
&\text{ClCH}_2\text{CH}_2\text{SiH}_3 \quad \beta\text{-chloroethylsilane} \\
&\text{(CH}_3\text{)}_2\text{(C}_2\text{H}_5\text{)}_2\text{Si} \quad \text{dimethyldiethylsilane}
\end{align*}
\]

**Esters of Orthosilicic Acid**

These compounds are regarded as products of the replacement of hydrogen atoms in \( \text{SiH}_4 \) by alkoxy or aryloxy groups.

The name of the esters is formed from the number and name of the organic atomic groups and the termination "silane".

For instance:

\[
\begin{align*}
&(\text{CH}_3\text{O})_4\text{Si} \quad \text{tetramethoxysilane} \\
&(\text{CH}_3\text{O})_2\text{Si(OCC}_2\text{H}_5\text{)}_2 \quad \text{dimethoxydiethoxysilane} \\
&(\text{CH}_3\text{O})_3\text{SiOC}_6\text{H}_5 \quad \text{trimethoxyphenoxysilane}
\end{align*}
\]

**Haloesters of Orthosilicic Acid**

The haloesters of orthosilicic acids are regarded as a product of substitution of one, two, or three hydrogen atoms in \( \text{SiH}_4 \) by alkoxy- or aryloxy groups with the simultaneous substitution of three, two, or one hydrogen atom in \( \text{SiH}_4 \) by like or unlike halogen atoms. The names of the haloesters are composed of the number and name...
of the organic groups, the number and name of the halogen atoms, and the termination "silane".

For example:

\[(\text{CH}_3\text{O})\text{SiCl} \quad \text{trimethoxychlorosilane}\]
\[(\text{CH}_3\text{O})(\text{C}_2\text{H}_5\text{O})\text{SiCl}_2 \quad \text{methoxyethoxydichlorosilane}\]

**Substituted Esters of Orthosilicic Acid**

The substituted esters of orthosilicic acid are considered as products of the substitution of one or several hydrogen atoms in \(\text{SiH}_4\) by like or unlike organic radicals, with the simultaneous substitution of other hydrogen atoms attached to the silicon by alkoxy or aryloxy groups. If the silicon atom is attached to one radical, then such compounds are called monosubstituted esters of orthosilicic acid, if with two radicals, disubstituted esters, etc.

The names of the substituted esters of orthosilicic acids are formed of the number and names of the organic radicals, the number and names of the alkoxy or aryloxy groups, and the termination "silane".

For example:

\[
\begin{align*}
\text{CH}_3\text{Si(OC}_2\text{H}_5\text{)}_3 & \quad \text{methyltriethoxysilane} \\
(\text{CH}_3)_2\text{Si(OC}_2\text{H}_5\text{)}_2 & \quad \text{dimethyldiethoxysilane} \\
\text{CH}_3\text{Si(OC}_2\text{H}_5\text{)}_2 & \quad \text{methylphenyldiethoxysilane} \\
\text{C}_6\text{H}_5\text{Si(OC}_2\text{H}_5\text{)}_2 & \quad \text{phenylphenyldiethoxysilane} \\
\text{ClC}_6\text{H}_5\text{Si(OC}_4\text{H}_9\text{)}_2 & \quad \text{methyl-4-chlorophenyldiethoxysilane} \\
\text{CH}_3\text{Si(OCH}_2\text{CH}_2\text{Cl)}_2 & \quad \text{methyl-2-chloroethyldi(2-chloroethoxy)silane} \\
\end{align*}
\]
The Alkyl-(Aryl-)-Halosilanes

The (alkyl)-halosilanes are regarded as the product of substitution of one, two, or three hydrogen atoms in silicon hydride, \( \text{SiH}_4 \), by organic radicals, with the simultaneous substitution of three, two, or one atom of hydrogen respectively, in the same silicon hydride, by halogen atoms. If the silicon atom is attached to one radical, then such compounds are called monoalkyl-(monocaryl)-halosilanes, if to two radicals, respectively dialkyl-(diaryl)-halosilanes, if with three radicals, trialkyl-(triaryll)-halosilanes. The position of the substituent in the aromatic radical is noted as follows:

![Diagram of an aromatic radical](image)

The names of the alkyl-(aryl-)-halosilanes are formed from the number and name of the organic radicals, the number and name of the halogens, and the termination "silane".

For example:

\[
\begin{align*}
\text{C}_6\text{H}_5\text{SiCl}_3 & \quad \text{phenyltrichlorosilane} \\
\text{CH}_3 & \\
\text{Cl} & \\
\text{SiCl}_2 & \\
\text{C}_1\text{H}_2 & \\
\text{Cl} & \\
\end{align*}
\]

\( \text{CH}_2\text{Cl} \quad \text{methyl-}(4\text{-chlorophenyl})-\text{dichlorosilane} \)

\( \text{ClCH}_2\text{CH}_2 \quad \text{p-chloroethyl-}(3\text{-chlorophenyl})-\text{dichlorosilane} \)

Hydroxyl-Derivative Organosilanes

The hydroxyl-derivative organosilanes are considered as products of the substitution of one, two, or three hydrogen atoms in the silicon hydride \( \text{SiH}_4 \) by...
organic radicals with the simultaneous substitution of three, two or one hydrogen atoms by hydroxyl groups. If one, two, or three hydroxyl groups are attached to the silicon atom, we distinguish mono-, di-, or trihydroxy-derivative silanes. The names of hydroxyl-derivative organosilanes are formed of the number of hydroxyl groups, called "hydroxy", the number and name of the organic radicals, and the termination "silane".

For example:

\[(\text{C}_2\text{H}_5)\text{Si(OH)}_2\quad \text{dihydroxydiethylsilane}\]
\[\text{CH}_3\text{Si(OH)}_2\quad \text{dioxymethylphenylsilane}\]
\[\text{C}_6\text{H}_5\quad \text{dihydroxyethyl-(4-chlorophenyl)-silane}\]
\[\text{C}_2\text{H}_5\quad \text{hydroxymethylethylphenylsilane}\]

**Alkyl-(Aril)-Aminosilanes**

Alkyl-(aryl)-aminosilanes are regarded as products of the substitution of one, two, or three hydrogen atoms in silicon hydride \(\text{SiH}_4\) by organic radicals, with the simultaneous substitution of three, two, or one hydrogen atoms in the same silicon hydride by amino groups, substituted amino groups, or by organic groups containing the amino group.

Mono-, di- and trialkyl-(triaryl)-amino silanes are distinguished, depending on the number of radicals in the molecule attached to the silicon atom. The names of alkyl-(aryl)-amino silanes are formed from the number and name of the amino groups or substituted amino groups, the number and name of the organic radicals, and the termination "silane".
For example:

\[
\begin{align*}
\text{CH}_3\text{Si(NH}_2)_2 & \quad \text{Diaminomethylphenylsilane} \\
\text{C}_6\text{H}_5 & \\
(\text{CH}_3)_3\text{SiNHCH}_3 & \quad \text{methylaminotrimethylsilane} \\
\text{CH}_3\text{Si(NH}_6\text{H}_5)_2 & \quad \text{di-}(\text{phenylamino})-\text{methylphenylsilane} \\
\text{C}_2\text{H}_5 & \\
(\text{CH}_3)_3\text{SiNHSi(CH}_3)_2 & \quad \text{hexamethyaminodisilane}
\end{align*}
\]

**Alkoxyl-(Arylox)-Aminosilanes**

Alkoxyl-(arylox)-aminosilanes are regarded as products of the substitution of one, two, and three hydrogen atoms in SiH\textsubscript{4} by alkoxyl-(arylox)-groups with simultaneous substitution of three, two, or one hydrogen atom by amino groups or substituted amino groups. The names of alkoxyl-(arylox)-amino silanes are formed from the number and names of the alkoxyl-(arylox)-groups, the number and name of the amino groups or substituted amino groups, and the termination "silane".

For example:

\[
\begin{align*}
\text{CH}_3\text{CHO-SiNH}_2 & \quad \text{isopropoxydibutoxyaminosilane} \\
\text{CH}_3 & \quad (\text{OC}_4\text{H}_9)_2 \\
(\text{CH}_3\text{H}_2\text{O-O-})_3\text{SiNH}_2 & \quad \text{tri-}(\text{tert-butoxy})-\text{aminosilane} \\
\text{CH}_3 & \\
\text{C}_2\text{H}_5\text{O}_2\text{Si(NHCH}_3)_2 & \quad \text{diethoxydi-(methylamino)-silane}
\end{align*}
\]

**Alkyl-(Aryl)-Aminohalosilanes**

Alkyl-(aryl)-aminohalosilanes are regarded as products of substitution of one, two, or three hydrogen atoms in SiH\textsubscript{4} by substituted amino groups with the simultaneous...
sous substitution of three, two, or one hydrogen atom, by halogens.

The names of alkyl-(aryl)-aminohalosilanes are formed from the number and name of the substituted amino groups, the number and name of the halogens, and the termination "silane".

For example:

\[
\begin{align*}
\text{C}_2\text{H}_5 \quad &\quad \text{NSiCl}_3 \quad \text{diethylaminotrichlorosilane} \\
\text{C}_2\text{H}_5 \quad &\quad \text{(C}_6\text{H}_5\text{NH})_2\text{SiCl}_2 \quad \text{di-(phenylamino)-dichlorosilane}
\end{align*}
\]

**Alkyl-(Aryl)-iminosilanes**

Alkyl-(aryl)-iminosilanes are regarded as products of the substitution of all the hydrogen atoms in silicon hydride \(\text{SiH}_4\) by imino groups \(-\text{NR}\), or of two hydrogen atoms by an imino group with the simultaneous substitution of the remaining hydrogen atoms by organic radicals, atom groups or other atoms. The names of these compounds are formed from the number and name of the organic radicals or groups, the number and name of the imino groups, and the termination "silane".

For example:

\[
\begin{align*}
\text{(C}_2\text{H}_5)_2\text{Si} = \text{NCH}_3 \quad &\quad \text{methyliminodiethylsilane} \\
\text{H}_5\text{C}_6\text{N} = \text{Si} = \text{NC}_6\text{H}_5 \quad &\quad \text{di-(phenylimino)}\text{-silane} \\
\text{(C}_6\text{H}_5\text{NH})_2\text{Si} = \text{NC}_6\text{H}_5 \quad &\quad \text{di-(phenylamino)-phenyliminosilane}
\end{align*}
\]

**Silicon Isocyanates**

Silicon isocyanates are regarded as products of the substitution of one, two, three, or four hydrogen atoms in silicon hydride \(\text{SiH}_4\) by the isocyanato group \(\text{N} = \text{C} = \text{O}\), and by the simultaneous substitution of three, two, or one hydrogen atom respectively in the same silicon hydride by an organic radical, a group, or another atom. The names of silicon isocyanates are made up of the number and name of the radicals, the groups, or of the other atoms, the number of isocyanato groups and the termination "silane".
tion "silane".

For example:

\[
\begin{align*}
(CH_3)_2Si(NCO)_2 & \quad \text{dimethyldiisocyanatosilane} \\
(C_2H_5O)_2Si(NCO)_2 & \quad \text{diethoxydiisocyanatosilane} \\
CH_3O \quad OC_6H_5 & \quad \text{methoxy-(phenoxy)-4-chlorophenylisocyanatosilane} \\
ClC_6H_4 & \quad \text{chloromethylmetoxy-4-chlorophenoxyisocyanatosilane}
\end{align*}
\]

**Silicon Isothiocyanates**

Silicon isothiocyanates are regarded as products of the substitution of one, two, three, or four hydrogen atoms in SiH\(_4\) by isothiocianato groups, and also by the simultaneous substitution of three, two, or one hydrogen atom by organic radicals, groups, or other atoms.

The names of silicon isothiocyanates are formed in the same way as the names of isocyanates, but instead of the word "isocyanato" the word "isothiocyanato" is used.

For example:

\[
(C_2H_5)Si(NCS)_3 \quad \text{ethyltriisothiocyanatosilane}
\]

\[
\begin{align*}
(C_2H_5)_2 & \quad \text{ethoxyisobutoxy-4-chlorophenylisothiocyanatosilane}
\end{align*}
\]

**Thioethers**

The thioethers are regarded as products of the substitution of one, two, three, or four hydrogen atoms in SiH\(_4\) by RS groups, together with the simultaneous substitution of one, two, or three hydrogen atoms in the same silicon hydrides by organic

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radicals, atomic groups, or other atoms. The names of thioethers are formed from
the number and name of the thio groups, the number and name of the radicals, groups
or other atoms attached to the silicon, and the termination "silane".

For example:

\[(C_2H_5)_3SiC_6H_5\] tri-(ethylthio)-phenylsilane
\[(BrC_6H_4S)_4Si\] tetra-(4-bromophenylthio)-silane
\[[\text{CH}_3\text{CS}]_2\text{Si}(C_6H_5)_2\] di-(tert-butylthio)-diphenylsilane

Low Molecular Organosiloxanes

On the condensation of organosilicon hydroxyl derivatives, compounds with mole-
cules containing the siloxane groups \(-\text{Si}-\text{O-Si-}\) are formed.

Compounds consisting of atoms of silicon and oxygen attached in succession to
each other, in which the silicon is also attached to organic radicals or groups, are
called organosiloxanes.

Compounds with a large number of organosiloxane groups are called polyorgano-
siloxanes.

Polyorganosiloxanes may be of linear or cyclic structure.

The names of low-molecular organosiloxanes are composed of the number indicat-
ing the position of the silicon atom in the chain or ring, the number and name of
the organic radicals or groups, the number of silicon atoms linked to each other
through oxygen, and the termination "siloxane".

For example:

\[
\begin{array}{cccc}
\text{C}_6\text{H}_5 & \text{CH}_3 & \text{C}_6\text{H}_5 & \text{CH}_3 \\
\text{C}_2\text{H}_5 & \text{Si} & \text{O} & \text{Si} \\
\text{CH}_3 & \text{C}_6\text{H}_5 & \text{CH}_3 & \text{C}_6\text{H}_5
\end{array}
\]

1, 4-diethyl-1, 2, 3, 4-tetra-
phenyl-1, 2, 3, 4-tetramethyl-
tetrasiloxane
In the case of a branched chain of an organosilicon compound, the name (which is formed according to the pattern above given) also contains the number of the silicon atom attached to the side siloxane chain, the number and name of the radicals connected with the side siloxane chain, and the word "siloxano".

For example:

\[
\begin{align*}
\text{1, 3-dimethoxy-1, 2, 3-tri-(m-chlorophenyl)-1, 2, 3-trimethyl-trisiloxane} \\
\text{1, 2-diphenyl-1, 2-dimethyl-1, 2-diethyl-disiloxane.}
\end{align*}
\]

The prefix "cyclo" is added to the name of cyclic organosiloxanes.

For example:

\[
\begin{align*}
\text{hexamethylocyclotrisiloxane} \\
\text{hexaethoxycyclotrisiloxane}
\end{align*}
\]
Low-Molecular Alkyl-(Aryl)-Polyorganosilanes

The names of compounds whose silicon atoms are linked with each other through divalent radicals or groups are formed from the number and name of the radicals or organic groups, the number and name of the divalent radical, the number of silicon atoms, and the termination "silane".

For example:

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 \\
\text{Si} & \quad \text{Si} & \quad \text{Si} & \quad \text{Si} & \quad \text{Si}
\end{align*}
\]

hexamethylethylenedisilane

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{Si-OH} \\
\text{Si} & \quad \text{Si} & \quad \text{Si} & \quad \text{Si} & \quad \text{Si} & \quad \text{Si} & \quad \text{Si} & \quad \text{Si} & \quad \text{Si-OH}
\end{align*}
\]

1, 3, 4-hexamethyl-2-methyltrimethylsiloxancyclotetrasiloxane

High-Molecular Organosilicon Compounds

The preparation of high-molecular organosilicon compounds has become, during the last two decades, the most important trend in the chemistry of organosilicon compounds. For further successful development, and to facilitate research in this field of chemistry, the material already accumulated must be systematised, and a nomenclature and classification of high-molecular organosilicon compounds must be worked out. At the present time the names of the high-molecular organosilicon compounds are formed without any definite system, and are very often arbitrary, and do
not reflect the chemical structure.

A.V. Topchiyev, in collaboration with the present author, (Bibl.55) has proposed basic principles of nomenclature and classification of high-molecular organosilicon compounds. The nomenclature proposed by us is based on the structure of the main chain of the macromolecule.

\[
\begin{array}{c}
H \\
H \\
H \\
H \\
H \\
\end{array}
\]

Polymeric silicon hydride, \(H-Si-\overset{\text{Si}}{\longrightarrow}-\overset{\text{Si}}{\longrightarrow}H\) is taken as the starting substance for the classification, and all the other high-molecular organosilicon compounds are regarded as its derivatives, that is, as substances formed by replacing hydrogen atoms in it by organic radicals or groups. Compounds of certain classes are regarded as products of the simultaneous substitution of the group \(Si-Si\) by \(Si-O-Si\), \(Si-R-Si\), (where \(R\) is a divalent radical), \(Si-NH-Si\), etc.

The names of high-molecular organosilicon compounds are formed from the number and name of the end groups; the number and name of the side radicals connected with the silicon atom or with other atoms of an elementary unit in the molecular chain; the number and name of the radicals or atomic groups entering into the chain of the macromolecule, and the termination "silane" or "siloxane". The presence of a large number of repeating units in the chain is denoted by the prefix "poly". For the end groups, their position with respect to the first and the last atoms, \(1\) and \(n\), is indicated. The names of copolymers are formed by analogy.

From our point of view it is advisable to divide high-molecular organosilicon compounds into the following classes.

**Silano-chain Polymers, or Alkyl-(Aryl)-Polysilanes**

The silano-chain polymers are compounds with a chain consisting of silicon atoms alone. Substances of this class are regarded as products of the substitution
of the hydrogen atoms in polymeric silicon hydride $H_3Si(-Si-Si-H)$ by organic radicals or organic groups. Their names are formed from the number and name of the end groups, the prefix "poly", the number and name of the radicals or groups in the elementary unit of the molecular chain, and the termination "silane".

For example:

For example:

- $H_3Si(-Si-(CH_3)_3Si-(CH_3)_3Si-H)$, 1, n-hexamethylpolydimethylsilane
- $H_3Si(-Si-(C_6H_5)_3Si-(CH_3)_3Si-H)$, 1, n-hexamethylpolyphenylmethylsilane
- $H_3Si(-Si-(C_6H_5)_3Si-(CH_3)_3Si-H)$, polycyclophenylmethylsilane

Carbosilano-Chain Polymers, or Organopolyalkyl-(Polaryl)-Silanes

The carbosilano-chain polymers are compounds with a chain consisting of carbon and silicon atoms.

Substance of this class are considered as products of substitution in polymeric silicon hydride $H_3Si(-Si-Si-H)$ of hydrogen atoms by radicals or groups and the simultaneous substitution of the Si-Si group by the Si-R-Si group, where R is a divalent alkyl or aryl radical. Their names are formed from the number and name of the end group, the prefix "poly", the number and name of the side radicals or groups of an elementary unit of the molecular chain, the name of the divalent organic radi-
cals entering into the chain of the macromolecule, and the ending "silane".

For example:

\[
\begin{align*}
\text{CH}_3^- & \quad \text{CH}_3^- & \quad \text{CH}_3^- \\
\text{CH}_3 - \text{Si}^- & - \text{CH}_3 - \text{Si}^- & - \text{CH}_3 - \text{Si}^- & - \text{CH}_3 \\
\text{CH}_3 & & \text{CH}_3 & & \text{CH}_3 \\
\end{align*}
\]

1, n-hexamethylpolydimethylmethylenesilane

\[
\begin{align*}
\text{CH}_3^- & \quad \text{CH}_3^- & \quad \text{CH}_3^- \\
\text{CH}_3 - \text{Si}^- & - \text{C}_2\text{H}_5 - \text{Si}^- & - \text{C}_2\text{H}_5 - \text{Si}^- & - \text{CH}_3 \\
\text{CH}_3 & & \text{C}_2\text{H}_5 & & \text{CH}_3 \\
\end{align*}
\]

1, n-hexamethylpolydiethylene-silane

\[
\begin{align*}
\text{CH}_3^- & \quad \text{CH}_3^- & \quad \text{CH}_3^- \\
\text{CH}_3 - \text{Si}^- & - \text{C}_2\text{H}_5 - \text{Si}^- & - \text{C}_2\text{H}_5 - \text{Si}^- & - \text{CH}_3 \\
\text{CH}_3 & & \text{C}_2\text{H}_5 & & \text{CH}_3 \\
\end{align*}
\]

1, n-hexamethylpolydimethylphenylene-silane

Oxysilano-Chain Polymers, or Polyorganosiloxanes

Polyorganosiloxanes are compounds whose macromolecules consist of a chain made up of alternate atoms of oxygen and silicon.

Substances of this class are considered as products of the substitution of hydrogen atoms in polymeric silicon hydride \( \text{H-Si} \longrightarrow \text{H-Si} \longrightarrow \text{Si-H} \) by radicals or groups, with simultaneous substitution of the Si-Si group by the Si-O-Si group. Their names are formed of the number and name of the end groups, the prefix "poly", the number and name of the radical and groups attached to the silicon atom in an elementary unit of the chain, the number of atoms of silicon in a unit of the chain, and the termination "siloxane".

For instance:

\[
\begin{align*}
\text{CH}_3^- & \quad \text{CH}_3^- & \quad \text{CH}_3^- \\
\text{CH}_3 - \text{Si}^- & - \text{O}^- \text{Si}^- & - \text{OS}^- \text{CH}_3 \end{align*}
\]

1, n-hexamethylpolydimethylsiloxane
Carbosiloxane—Chain Polymers, or Polyorganalkylene—(Phenylene)—Siloxanes

Carbosiloxane-chain polymers are compounds with a chain consisting of atoms of carbon, silicon and oxygen.

Substances of this class are considered as products of the substitution of hydrogen atoms in polymeric silicon hydride $H-Si-\cdots-Si-H$ by organic radicals $H \cdots H$ or groups, with simultaneous substitution of the Si—Si groups by the Si—R—Si—O—Si
group (where \( R \) is an organic divalent radical). Their names are composed of the number and name of the end group, the prefix "poly", the number and name of the side radical and groups attached to the silicon in a unit of the chain, the name of the divalent radical entering into the chain of the macromolecule, the number of silicon atoms in a unit of the chain, and the termination "siloxane".

For example:

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH} \quad \text{CH}_2 \quad \text{CH}_3 \\
\text{CH}_2 \text{Si}- & \quad \text{Si}-\text{O}-\text{Si}- \quad \text{Si}-\text{CH}_2 \\
& \quad \text{CH}_3 \quad \text{CH}_2 \quad \text{CH}_3 \\
& \quad \text{CH}_3 \\
\end{align*}
\]

1, n-hexamethylpolytetramethyl-phenylenedisiloxane

\[
\begin{align*}
\text{CH}_2 \text{O} & \quad \text{CH}_3 \quad \text{CH}_2 \quad \text{OCH}_3 \\
\text{CH}_2 \text{O}-\text{Si} & \quad -\text{CH}_2-\text{Si}-\text{O}-\text{Si}- \quad -\text{Si}-\text{CH}_2-\text{OCH}_3 \\
& \quad \text{CH}_3 \quad \text{CH}_2 \quad \text{OCH}_3 \\
& \quad \text{CH}_3 \\
\end{align*}
\]

1, n-hexamethoxypolytetramethyl-methylenedisiloxane

**Metalloxysilano-Chain Polymers, or Polyorganometallosiloxanes**

Metalloxysilano-chain polymers are compounds with a chain consisting of atoms of divalent or polyvalent metals (magnesium, aluminum, chromium, lead, tin, etc.), oxygen and silicon.

The structure of the chain of the molecule may be expressed as follows:

\[
\begin{align*}
\text{R} & \quad \text{R} & \quad \text{R} \\
& \quad \text{Si}-\text{O}-\text{Si}-\text{O} \quad \text{M} \quad \text{Si}- \\
& \quad \text{R} & \quad \text{R} & \quad \text{R}
\end{align*}
\]

Compounds of this class are considered as products of the replacement of hydrogen atoms in polymeric silicon hydride \( \text{H-Si} \quad \text{Si} \quad \text{Si-H} \) by radicals or groups, and a simultaneous substitution of the \( \text{Si-Si} \) group by the \( \text{Si-O-M-O-Si} \) group. Their names are formed from the names and number of the end groups, the prefix "poly".
the number and name of the radicals or groups attached to the silicon or metals in the unit of the polymer chain, the name of the metal in the chain of the macromolecule, and the termination "siloxane".

For example:

\[
\text{C}_1\text{Cl}^{-}\text{C}_1\text{Cl}^{-}\text{C}_1\text{Cl}^{-}\text{C}_1\text{Cl}^{-}\text{C}_1\text{Cl}^{-}\text{C}_1\text{Cl}^{-}
\]

(1, n)-hexamethylpolyaluminoxydimethylsiloxane

\[
\text{O}_2\text{H}_5\text{OC}_2\text{H}_5\text{OC}_2\text{H}_5\text{OC}_2\text{H}_5
\]

(1, n)-hexaethoxypoly magnesiumoxydiethoxy siloxane

**Metalloidosilano Chain Polymers**

Metalloidosilano-chain polymers are compounds with molecular chains consisting of atoms of silicon and nitrogen, oxygen, or other metalloids, phosphorus, sulfur, etc.

Compounds of this class are considered as products of the replacement of hydrogen atoms in polymeric silicon hydride \( \text{H-Si}^{-} \text{Si}-^\text{Si-H} \) by radicals or groups, and the simultaneous replacement of the \( \text{Si-Si} \) groups by \( \text{Si-O-Si} \), \( \text{Si-NH-Si} \), \( \text{Si-O-P-O-Si} \), or by other groups.

The names of compounds of this class are formed from the name and number of the end groups, the prefix "poly", the number and name of the radicals and groups attached to the silicon or metalloid atoms in the unit of the polymer chain, and the name of the atoms and metalloid groups of which the chain of the macromolecule is composed.

For example:
CH₃-Si-NH-Si-NH-Si-CH₃
1, n-hexamethyldimethylaminosilane

CH₃-Si-O-P-O-Si-O-Si-CH₃
1, n-hexamethyldimethylphosphorodimethylsiloxane

CH₃-Si-N-Si-N-Si-CH₃
(l, n)-hexamethyldimethylphenylaminosilane

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CHAPTER I

COMPOUNDS OF SILICON AND HYDROGEN

The Saturated Silanes

The structure of the saturated silanes, \( \text{Si}_n\text{H}_{2n+2} \), corresponds to the structure of the hydrocarbons of the methane series, but the highest compound of the silane series that workers have been able to investigate has been hexasilane, \( \text{Si}_6\text{H}_{14} \). With great difficulty molecules of polysilanes with as many as 14 silicon atoms were prepared, but they could not be studied, owing to the very low stability of the silanes, which decreases with increasing number of silicon atoms in the molecule. All the known and studied saturated silanes are substances that easily ignite spontaneously in the air.

Of the saturated silanes, compounds from \( \text{SiH}_4 \) to \( \text{Si}_6\text{H}_{14} \) have been studied.

Monosilane \( \text{SiH}_4 \) has been prepared by electrolysis of a sodium chloride solution (with an \( \text{Al}_4\text{Si}_3 \) anode).

Disilane \( \text{Si}_2\text{H}_6 \), trisilane \( \text{Si}_3\text{H}_8 \), tetrasilane \( \text{Si}_4\text{H}_{10} \), pentasilane \( \text{Si}_5\text{H}_{12} \) and hexasilane \( \text{Si}_6\text{H}_{14} \) have been prepared (Bibl.2) by the action of mineral acids on magnesium silicide \( \text{Mg}_2\text{Si} \) and calcium silicide \( \text{Ca}_2\text{Si} \).

Methods of Preparation

One of the simplest methods of preparing a mixture of silanes is the decomposition of metallic silicides by mineral acids. The silicides of metals are obtained by high temperature roasting of amorphous or crystalline silicon or silicon dioxide,
or of certain silicates, with salts of metals, mainly of the second group.

Many different methods of preparing silicides have been described, but those of Kolbe, Kautski, as well as that of Stock and Somieskiy (Bibl.3) are of the greatest interest.

Magnesium silicide is formed when a mixture of MgCl₂, Na₂SiF₆, and NaCl is heated to a bright red heat. The silicides so obtained are a black mass with a grayish shade, in which leaflets and bright globules of black are distributed. From a mixture of CaCl₂, K₂SiF₆ and NaCl, calcium silicide was prepared in dark blue crystals in the form of shining plates, which in time grow dull in the air.

When a silicide is prepared by roasting a mixture of pure silicon dioxide and magnesium, it has been found that if the ratio SiO₂:Mg exceeds 1:2, then decomposition of the silicide so formed by acids does not liberate silanes, but only hydrogen. It was also found that on decomposition of magnesium silicide a substance of the composition Si₂H₂O₃ was formed as a solid insoluble precipitate. The silicides of magnesium and calcium may have a different composition. The literature states that the magnesium silicide Si₂Mg₅ prepared by Wohler consists of two silicides:

\[ 3 \text{Si}_2\text{Mg}_5 = 4 \text{Mg}_3\text{Si} + \text{Mg}_3\text{Si}_2 \]

On decomposition of Mg₃Si by HCl, silicoxymonohydrate is formed and hydrogen is evolved:

\[ 2\text{Mg}_3\text{Si} + 12\text{HCl} + 3\text{H}_2\text{O} = \text{Si}_2\text{H}_4\text{O}_3 + 6\text{MgCl}_2 + 8\text{H}_2 \]

When a mixture of silicon and magnesium is heated in a jet of hydrogen, eutectic mixtures are formed in which both components are soluble in any proportions. A number of investigators have reached the conclusion that magnesium silicide is a mixture of many silicides.

The quantity of silane liberated on the decomposition of calcium silicides depends on the ratio of the molten calcium and silicon. Thus, for instance, silicides
containing 38 - 52% of silicides liberate appreciably less silanes than silicides containing 60 - 91% of silicon.

The calcium silicides have been studied in detail by Koll* (Bibl.3). According to his researches, the simple formula Ca₂Si does not correspond to the experimental data. By modifying the conditions of separation of calcium silicides, he obtained two products.

1. A dark blue powder Ca₆Si₁₀ (mp 2000°С). The structural formula of this compound is:

   \[
   \begin{array}{c}
   \text{Si-Si-Si-Si-Si-Si-Si-Si-Si} \\
   \text{Ca Ca Ca Ca Ca Ca Ca Ca}
   \end{array}
   \]

2. A flocculent powder Ca₁₁Si₁₀

   \[
   \begin{array}{c}
   \text{Ca-Si-Si-Si-Si-Si-Si-Si-Si-Si-Si-Si} \\
   \text{Ca Ca Ca Ca Ca Ca Ca Ca Ca Ca Ca}
   \end{array}
   \]

The formation of a complex mixture of various products on the decomposition of silicides serves as a proof that the formula

   \[\text{Ca₅Si + 4HCl = SiH₄ + 2CaCl₂}\]

does not reflect the actual course of the process.

In the solid residue, besides silicomonooxyhydrate, a series of polymeric hydrides (SiH)_x and polymers of the composition (H₂SiO)_n were found. It may be assumed that the reaction proceeds in several stages, since silicomonooxyhydrate cannot be formed as a result of the primary reaction.

Under the action of sulfuric, nitric and acetic acids on calcium silicides, they are decomposed, with the formation of silicone and leucone. Silicone is formed on the decomposition of calcium silicide in the dark; it has the form of bright orange crystals and is easily oxidised on heating to silicon dioxide (Bibl.5).
D.I. Mendeleev called silicone chryson, because of its golden color. The elementary composition of silicone is \( \text{Si}_2\text{O}_2\text{H}_2 \); it is considered as the hypothetical hydrate of silicon suboxide, \( \text{Si}_2\text{OH}_2\text{O} \). Leucone is formed by the action of light on silicone. It is prepared by the action of dilute acids on calcium silicide in the light, and silicon hydrides are also formed during this reaction.

The chemical composition of the leucones correspond to the formula \( \text{Si}_4\text{O}_5\text{H}_3 \) (or \( \text{Si}_4\text{O}_5\text{H}_2 \)).

It is believed that at the beginning of the decomposition reaction a silicide complex is formed according to the equation

\[
\text{Mg}_2\text{Si} + 2\text{HCl} \rightarrow \text{Mg}_2\text{Si(OH)}_2
\]

and then that this complex then reacts with the acid, forming the hypothetical* silene:

\[
\text{H}_2\text{Si(OH)}_2 + 4\text{HCl} \rightarrow 2\text{MgCl}_2 + 2\text{H}_2\text{O} + \text{H}_2 + [\text{SiH}_4]
\]

which is afterward polymerized, and the polymers, on reacting with water, form various silanes (Bibl.6)

\[
(\text{SiH}_3)_2 + \text{H}_2\text{O} \rightarrow \text{H}_4\text{SiO} + \text{SiH}_4
\]

Prosiloxane \( \text{H}_2\text{SiO} \), according to the data of Stock and Somieski, was isolated in the monomeric form, which partially confirms the above formula for the reaction (Bibl.7).

The process of decomposition of the silicide was conducted in two stages. At first the silicide was subjected to the action of acid in the cold. In this case the greatest quantity of gases containing a mixture of silanes was evolved, while

*Monosilene \( \text{SiH}_2 \) has never been isolated, and its existence can only be supposed, but its formation as an intermediate reaction product is entirely possible.
the residue consisted of a fusible brown mass from which hydrogen was evolved. On heating this mass, the decomposition was completed, and in the residue a perfectly white mass termed by the author "silicoxalic acid" was formed.

In the study of this process it was postulated that the liquid reaction product might also contain higher compounds of the series $\text{Si}_n\text{H}_{2n+2}$, with a number of silicon atoms greater than six, but it was not possible to isolate them.

**Physical Properties**

The physical properties of the saturated silanes resemble those of the lower paraffins. Monosilane $\text{SiH}_4$ and disilane $\text{Si}_2\text{H}_6$ at room temperature are gases with a disagreeable odor at room temperature. In the absence of moisture and oxygen, they are rather stable.

Trisilane $\text{Si}_3\text{H}_8$ and tetrasilane $\text{Si}_4\text{H}_{10}$ are mobile, volatile, toxic liquids with an even more unpleasant odor than the lower compounds of the silane series. Pentasilane $\text{Si}_5\text{H}_{12}$ and hexasilane $\text{Si}_6\text{H}_{14}$ are also volatile liquids. They are extremely unstable; and their properties have not been studied in more detail.

The silanes are soluble in alcohol, benzine, tetra-substituted silanes and carbon disulfide. Solutions of silanes in carbon disulfide are highly explosive - the entrance of air into a closed vessel with such a solution leads to an explosion of great violence.

Table 3 gives the physical properties of the lower silanes, and, for comparison, the properties of the corresponding hydrocarbons.

**Table 3**

**Physical Properties of the Lower Silanes and Corresponding Hydrocarbons (Bibl.11)**

<table>
<thead>
<tr>
<th>Formula</th>
<th>Specific Gravity in Liquid State</th>
<th>Melting Point $^\circ\text{C}$</th>
<th>Boiling Point $^\circ\text{C}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{SiH}_4$</td>
<td>0.58(-185$^\circ$)</td>
<td>-185</td>
<td>-112</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Formula</th>
<th>Specific Gravity in Liquid State</th>
<th>Melting Point °C</th>
<th>Boiling Point °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>0.415 (-164°)</td>
<td>-182.5</td>
<td>-161.6</td>
</tr>
<tr>
<td>Si₂H₆</td>
<td>0.686 (-25°)</td>
<td>-132</td>
<td>-44</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0.546 (-88°)</td>
<td>-182.8</td>
<td>-88.6</td>
</tr>
<tr>
<td>Si₃H₈</td>
<td>0.743 (0°)</td>
<td>-117</td>
<td>-53</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>0.585 (-44°)</td>
<td>-187.6</td>
<td>-42.1</td>
</tr>
<tr>
<td>Si₄H₁₀</td>
<td>0.825 (0°)</td>
<td>-90</td>
<td>-109</td>
</tr>
<tr>
<td>C₄H₁₀</td>
<td>0.60 (0°)</td>
<td>-138.3</td>
<td>-0.5</td>
</tr>
</tbody>
</table>

The data of Table 3 shows that the density of the silanes is considerably greater than that of the corresponding hydrocarbons. The melting points and boiling points of the silanes increases more sharply with increasing molecular weight than the melting and boiling points of the corresponding hydrocarbons.

The interatomic distance between the hydrogen and carbon atom in methane is 1.093 Å, while that between the hydrogen and silicon in silane is 1.54 Å.

**Chemical Properties**

The most characteristic feature of the silanes is their oxidizability. Oxidation, depending on the conditions, is either violent, leading to the formation of SiO₂, or quiet, leading to the formation of a number of intermediate oxidation products.

The oxidation of trisilane, tetrasilane, pentasilane, and hexasilane has been little studied owing to the intensity of the reactions, which take the course of violent explosion.

The admixture of even negligible quantities of pentasilane in the lower silanes increases the possibility of explosion and intensifies such explosion. For this reason all studies of the silanes must be conducted very cautiously, and the maximum purity of the product must be attained. The entrance of even insignificant quanti-
ties of air in vessels containing silane is particularly dangerous. The so-called "harmful space" must also be avoided.

Monosilane, in presence of oxygen, is oxidized explosively even at the temperature of liquefaction of air (−191°C). In oxygen diluted with nitrogen or argon in vacuo at a temperature of 70 - 80°C, oxidation was still rather intense, and toward the end of the process the oxygen disappeared completely from the gaseous medium. In the reaction vessel, after the completion of the reaction, were found, in addition to the inert gas, hydrogen, water, the gaseous oxidation product, and a white or brown solid substance.

Studies of this solid substance showed it to consist of a complex compound, which was a polymer of the silicon analog of formic anhydride or polymeric prosilane:

\[ \{[\text{SiH}_2(0)]_20\}_x \quad \text{polymer of silicon analog of formic anhydride} \]

In the reaction vessel, after the completion of the reaction, were found, in addition to the inert gas, hydrogen, water, the gaseous oxidation product, and a white or brown solid substance.

With an excess of oxygen, the oxidation of the silanes is accompanied by an explosion. The cause of the explosion is the explosion of a mixture of oxygen and hydrogen, since hydrogen is liberated during the oxidation. According to the data of researches of Stock and Somieski (Bibl.3), the oxidation of silanes leads to the formation of polymeric products.

Owing to their easy oxidizability, the silanes are good reducing agents. They reduce KMnO₄ to MnO₂, Hg⁺⁺ to Hg⁺, Fe⁺⁺⁺ to Fe⁺⁺, Cu⁺⁺ to Cu⁺. The reduction of silver by silanes from a concentrated AgNO₃ solution takes place in several stages:

\[ \text{SiH}_4 + 4\text{AgNO}_3 \rightarrow \text{SiAg}_4 + 4\text{HNO}_3 \]

\[ 4\text{AgNO}_3 + \text{SiAg}_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 8\text{Ag} + 4\text{HNO}_3 \]

The silanes also reduce K₂Cr₂O₇, CuSO₄, HgCl₂, AuCl₃, etc.

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The silanes, especially the higher homologs, decompose even when stored in a place completely free of air and light. The decomposition takes place with formation of both lower silanes and polymers. A solid residue \((\text{SiH}_2)_x\) is always formed in this transformation. On heating, the decomposition is accelerated. Monosilane is most stable of all. When it is dissolved in a medium completely free of oxygen and air, its decomposition begins only at \(400^\circ\text{C}\). Disilane decomposes at \(250^\circ\text{C}\). The other compounds of the silanes series begin to decompose in the light at already \(0^\circ\text{C}\).

When tetrasilane is kept for a month under conditions preventing contact with air, 20% of hydrogen is liberated, and 16% of mono- and disilanes, together with a little trisilane is formed. The penta and hexasilanes decompose to the extent of 85 - 90% in a few months. Their decomposition products consists of a mixture of gaseous \(\text{SiH}_4\) and \(\text{Si}_2\text{H}_6\) with a certain quantity of \(\text{Si}_3\text{H}_8\), \(\text{Si}_4\text{H}_{10}\), and the solid polymer \((\text{SiH}_2)_x\).

The silanes are decomposed more completely and considerably faster by water. The decomposition is so complete that the volumetric measurement of the quantity of hydrogen evolved is used for analysis.

\[
\begin{align*}
\text{SiH}_4 + 2\text{H}_2\text{O} & = \text{SiO}_2 + 4\text{H}_2 \\
\text{Si}_2\text{H}_6 + 4\text{H}_2\text{O} & = 2\text{SiO}_2 + 7\text{H}_2 \\
\text{Si}_3\text{H}_8 + 6\text{H}_2\text{O} & = 3\text{SiO}_2 + 10\text{H}_2 \\
\text{Si}_4\text{H}_{10} + 8\text{H}_2\text{O} & = 4\text{SiO}_2 + 13\text{H}_2
\end{align*}
\]

The decomposition of silanes of different molecular weight by water takes place at a different rate. Thus, for example, \(\text{SiH}_4\) is 15 - 20% decomposed in 24 hours, \(\text{Si}_2\text{H}_6\) 20 - 25% in the same time, and \(\text{Si}_3\text{H}_8\) - 30%.

When the silanes are decomposed by water, together with \(\text{SiO}_2\), a completely insoluble transparent film is formed on the walls of the vessel. This consists of a polymer having the structure of a polysiloxane. This film is found only when no
mercury adheres to the walls of the vessel after the experiment.

It has also been found that the silanes are not decomposed by chemically pure water in a quartz vessel. It has been established that the alkalinity of the glass is of great importance in the decomposition of the silanes by water. The reaction of pure silicon with water likewise fails to proceed in the absence of alkali. The alkali is believed to have a catalytic action.

\[
\begin{align*}
\text{Si} + 2\text{NaOH} + \text{H}_2\text{O} & \rightarrow \text{Na}_2\text{SiO}_3 + 2\text{H}_2; \\
\text{Na}_2\text{SiO}_3 + \text{H}_2\text{O} & \rightarrow \text{SiO}_2 + 2\text{NaOH}
\end{align*}
\]

A detailed study of the action of alkalies on silanes has shown that dry alkali, just like chemically pure water, has practically no action in decomposing silanes. Under the action of aqueous solutions of alkalies on silanes, this reaction proceeds rapidly and to completion. A 33\% aqueous solution of NaOH acts most powerfully at all, completely decomposing monosilane in two hours, disilane in one hour, and the other silanes in a few minutes.

\[
\begin{align*}
\text{SiH}_4 + 2\text{NaOH} + \text{H}_2\text{O} & = \text{Na}_2\text{SiO}_3 + 4\text{H}_2; \\
\text{Si}_2\text{H}_6 + 4\text{NaOH} + 2\text{H}_2\text{O} & = 2\text{Na}_2\text{SiO}_3 + 7\text{H}_2; \\
\text{Si}_3\text{H}_8 + 6\text{NaOH} + 3\text{H}_2\text{O} & = 3\text{Na}_2\text{SiO}_3 + 10\text{H}_2; \\
\text{Si}_4\text{H}_{12} + 8\text{NaOH} + 4\text{H}_2\text{O} & = 4\text{Na}_2\text{SiO}_3 + 13\text{H}_2
\end{align*}
\]

In the absence of water, the silanes probably form intermediate products with an alkali. These products are decomposed under the action of water, liberating hydrogen and forming silicates. There are still no trustworthy data confirming this view.

When silanes react with halogens, all the hydrogen atoms are completely and instantaneously replaced by halogen atoms. The reaction proceeds explosively. The hydrohalogen acids do not react with silanes at high temperatures (up to 200\°C), but in the presence of AlCl\(_3\) this reaction proceeds at a marked speed at 100\°C. The hydrogen atoms are replaced by halogens. In this way monochlorosilane H\(_2\)SiCl, dichlorosilane H\(_2\)SiCl\(_2\), monobromosilane H\(_2\)SiBr, dibromosilane H\(_2\)SiBr\(_2\), etc., have been prepared, as well as the halo-derivatives of disilane.
Bromine and nitric acid decompose disilane and the higher silanes. Sulfuric acid has no action on silanes. The chlorine and fluorine derivatives of methane react explosively with silanes. The interaction of silanes with chloroform and carbon tetrachloride has been studied in detail. The reaction does not proceed in the absence of traces of oxygen, but it does proceed explosively in cases where there are traces of oxygen in the reaction vessel. It has also been found that even in the absence of traces of oxygen, chloroform reacts with trisilane at 60 - 70°C in the presence of AlCl₃. The reaction proceeds rapidly, but with no flash or explosion. The reaction product consists of derivatives of trisilane of various degrees of chlorination, and of dichloromethane.

\[
\begin{align*}
\text{Si}_2\text{H}_6 + 4\text{HCCl}_3 & = \text{Si}_2\text{H}_4\text{Cl}_4 + 4\text{CH}_2\text{Cl}_2 \\
\text{Si}_2\text{H}_6 + 5\text{HCCl}_4 & = \text{Si}_2\text{H}_5\text{Cl}_5 + 5\text{CH}_2\text{Cl}_2 
\end{align*}
\]

THE UNSATURATED SILANES

The unsaturated silanes, the silenes \( \text{Si}_n\text{H}_{2n} \) and the silines \( \text{Si}_n\text{H}_{2n-2} \), correspond in structure to the unsaturated hydrocarbons of the ethylene and acetylene series. The unsaturated silines have not yet been isolated by anyone in the monomeric form. From compounds of this class, polymeric unsaturated silane \( (\text{SiH}_2)_x \) has been obtained.

The Silenes \( \text{Si}_n\text{H}_{2n} \)

The existence of monosilene \( \text{SiH}_2 \) is recognized as possible, as already stated, only as an intermediate product in the decomposition of the silicides and the formation of saturated silanes. In this case monosilene is polymerized to the solid product \( (\text{SiH}_2)_x \).

Stock and Somieski (Bibl.7) postulate that monosilene is formed as an intermediate product on the reaction of monochloro- or dichlorosilane with sodium amalgam.
\[ \text{SiH}_2\text{Cl}_2 + 2\text{Na} = \text{H}_2\text{SiNa} + 2\text{NaCl} \]
\[ \text{H}_2\text{SiNa} + \text{Hg} = \text{H}_2\text{Si} + \text{HgNa}_2 \]

The \( \text{H}_2\text{Si} \) so formed is polymerized.

Monosilsilene is the hydride of silicon suboxide \( \text{SiO} \). An indirect proof of the existence of this intermediate product (monosilene) is the isolation by Friedel and Landenburg of the subiodide \( \text{SiI}_3 \), which is a derivative of \( \text{SiH}_2 \).

There are various views on the possibility of preparing silicoethylene. The hypothesis has been expressed that \( \text{Si}_2\text{H}_4 \) can be obtained from the gaseous product of the decomposition of magnesium silicide by HCl by liquefying these products with liquid air. After fractionation of the condensate at room temperature and distilling off the \( \text{SiH}_4 \) and \( \text{Si}_2\text{H}_6 \), a liquid of boiling point 60°C remains behind, which explodes violently in the presence of oxygen. This liquid was considered to be silicoethylene. The same liquid was also obtained on the decomposition of calcium silicide.

Other investigators (Bibl.8) categorically deny the existence of silicoethylene, and consider the liquid so obtained to be a mixture of silenes. With the object of verifying the existence of siliconethylene, a series of experiments in its isolation by cleavage of water from disiloxane was performed.

\[ \text{H}_2\text{Si}--\text{O}--\text{SiH}_3 \rightarrow \text{H}_2\text{O} \cdot 2\text{SiH}_3 \]

All experiments in heating disiloxane led to the polymerization of the product, while experiments with dehydrating agents of the type of \( \text{P}_2\text{O}_5 \) led to the liberation of monosilane.

Thus the attempts to isolate silicoethylene in the monomeric state were unsuccessful.

The hypothesis that silicoethylene exists only in the polymeric form must be considered to be most probable.

Other representatives of this series of compounds are unknown.
The Silines $\text{Si}_n\text{H}_{2n-2}$

Up to the present time no one has succeeded in preparing silines, and their derivatives are also unknown.

Polymeric compounds corresponding to the general formula $\text{Si}_n\text{H}_{2n-2}$ or close to it, judging by the results of elementary analyses, were isolated by Bertlo (Bibl.9) on the decomposition of monosilane in a bomb. A dark solid substance was found on the walls of the bomb after the reaction. This solid substance, according to the results of the analysis, has the following composition: $\text{SiH}_{1.42}; \text{SiH}_{1.43}; \text{SiH}_{1.56}; \text{SiH}_{1.58}$ or $(\text{Si}_2\text{H}_3)$.

It is believed that on treatment of calcium silicide with dilute acids, silicoacetylene is given off. The product so obtained is a polymeric yellow crystalline explosive substance. The basis for the assertion that it is polymeric silicoacetylene is only the formula of the elementary composition of the substance obtained. On heating in air the product is oxidized, while on heating in a tube it is decomposed into Si and $\text{H}_2$. By decomposing other silicides (for instance, barium and strontium silicides), a substance similar to that described could not be isolated.

The unsaturated polymeric hydrides $(\text{SiH})_x$ are formed, as already stated, on the spontaneous decomposition of the higher silanes, and also on the decomposition of the silicides (Bibl.10).

When chlorides of monosilane react with sodium amalgam, unsaturated hydrides in the form of a gray powder are formed. The hydrides are also obtained on the decomposition of a mixture of silanes. The residual viscous greasy mass liberates $\text{SiH}_4$, $\text{Si}_2\text{H}_6$ and hydrogen. Further distillation of the mass, after long standing, leads to the formation of a porous yellow amorphous residue. The solid product has the following elementary composition: $\text{SiH}_{1.22}; \text{SiH}_{1.15}; \text{SiH}_{1.14}; \text{SiH}_{1.13}; \text{SiH}_{1.12}$.

The action of very dilute alkali on the polymeric hydrides leads to the evolution of hydrogen and $\text{SiH}_4$. By the action of a KOH solution the hydrides are decomposed into hydrogen and $\text{SiO}_2$, like all silanes.
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2. Moissant - Compt. rend., 134, 569 (1902)
4. Gauthier, S. - 1041 (1865)
6. Schwarz, R. - Ber., 55, 3242 (1922)
7. Stock, A. and Somieski, C. - Ber., 56, 267 (1923); 56, 139 (1923)
CHAPTER II

COMPONDS OF SILICON WITH HALOGENS

The preparation and a few properties of the haloderivatives of silicon were described as early as last century. This class of compounds includes the haloderivatives of monosilane, i.e., mono-, di-, tri- and tetrahalosilanes (general formula \( \text{H}_n\text{SiX}_{4-n} \), where \( n = 0, 1, 2, \) and \( 3 \)), and of the haloderivatives of polysilanes (general formula \( \text{Si}_m\text{H}_{n}\text{X}_{2m+2-n} \), where \( m \) may be as high as \( 10 \)).

The haloderivatives of polysilanes are of no practical importance today and have been studied considerably less than the haloderivatives of monosilane.

The stability of the silanes is increased considerably by the introduction of halogens into their molecules. The higher silanes, even after the introduction of only a single halogen atom, can be distilled in vacuo without decomposing. The halo-substituted silanes, regardless of the nature of the halogens and their number, possess the typical properties of halo-anhydrides: they easily exchange their halogens for hydroxyl, with water and hydroxyl-containing compounds. When halosilanes react with organometallic compounds, unsaturated hydrocarbons, or diazo compounds, the halogen atoms are easily replaced by organic radicals. The halosilanes are not reduced to silanes, and, in contrast to the haloderivatives of hydrocarbons, they do not form organomagnesium compounds. Here the peculiarities of silicon are manifested, which, as already stated earlier, has a greater affinity for the metalloids than for the metals. Tetrahalosilanes, under the action of water, form the unstable and readily condensed orthosilicic acid. The trihalosilanes \( \text{HSiX}_3 \) form easily condensed
trihydroxysilanes. Under the action of water in an alkaline or acid medium, reaction takes place, with evolution of hydrogen, as a result of the replacement of hydrogen by hydroxyl.

Under the action of water on dihalosilanes $\text{H}_2\text{SiCl}_2$ and monohalosilanes $\text{H}_3\text{SiCl}$, the halogens contained in them are replaced by hydroxyl, thus forming the corresponding dihydroxysilanes and hydroxysilanes. The trihydroxyl silanes, dihydroxyl silanes and hydroxysilanes are of a structural analogous to that of the alcohols, but differ in their properties from the alcohols by their exceptional tendency to form polymers.

The haloderivatives of the monosilanes are important starting substances for the synthesis of organosilicon monomers and polymers.

**Tetrahalosilanes**

The most important representative of the tetrahalosilanes is silicon tetrachloride. The great importance of $\text{SiCl}_4$ is due to the simplicity of its preparation, its inexpensiveness, and the availability of the raw materials for its synthesis, so that the cost of $\text{SiCl}_4$ is many times lower than the cost of all other halo-derivatives of silicon. Besides this, silicon tetrachloride, in its chemical properties (for instance the ease of esterification), has the advantage over the other halodisilanes. Its industrial production has therefore been widely developed in a number of countries.

**Methods of Preparing Silicon Tetrachloride**

The synthesis of silicon tetrachloride is most often conducted according to the formula

$$\text{Si} + 2\text{Cl}_2 \rightarrow \text{SiCl}_4$$

Silicon tetrachloride was first prepared by the action of chlorine on silicon at a red heat as long ago as 1824. This reaction was later studied by a number of
investigators (Bibl.1, 2).

A detailed study of the chemical process of preparing silicon tetrachloride by the action of the halogen on an alloy of silicon with iron is given in one of my own works (Bibl.3).

The raw material for the synthesis of silicon tetrachloride is ferrosilicon (containing not less than 35% of silicon) which is ground into lumps 1 to 2 cm in size and is charged into a reaction tube placed in a furnace. The tube is heated only at the beginning of the process. When a temperature of 200°C is reached, the heat is shut off and a stream of dry chlorine is passed through the tube. The temperature of the reaction mixture rises to 450 – 600°C (since the reaction is exothermic) and is maintained within these limits by regulating the rate of flow of the chlorine.

The yield of silicon tetrachloride depends on the temperature of chlorination (Fig.1) of 500°C. Above 500°C the yield does not vary; SiCl₄ boils at 57.7°C and is separated from the byproduct of the reaction, ferric chloride, by simple distillation. If chlorination is conducted at temperatures of 300 – 350°C, the product of chlorination contains, in addition to the silicon tetrachloride, a small quantity of high-boiling silicon chlorides, hexachlorodisilane Cl₃SiSiCl₃ and octachlorotrisilane Cl₃SiCl₂SiCl₃.

On further lowering of the reaction temperature, the content of polychlorosilanes in the product increases, amounting at 200°C to 0.4% of the weight of the con-
densate, and at 180°C, to 5.7%. In 1913, Martin (Bibl.2) proposed a system for the process of chlorination, that has not encountered any objections down to recent times. Martin supposes that the atoms of silicon are bound by the forces of the principal valences in silicon and its alloys, including ferrosilicon. When it reacts with chlorine, the bonds of the silicon are broken during the first instant, chlorine atoms become attached to it, and linear polymeric molecules of chlorosilanes are formed, which, under the subsequent action of chlorine are broken, thus forming chlorosilanes of lower molecular weight.

This process ends with the formation of silicon tetrachloride.

The stability of the higher chlorosilanes decreases sharply with increasing temperature, and therefore their content in the condensate is considerably reduced when the temperature of the synthesis is raised. An additional confirmation of the Martin mechanism is the fact that at the initial instant of chlorination at low temperatures, the higher chlorosilanes and silicon tetrachloride are obtained.

Another group of methods for preparing silicon tetrachloride is based on the reduction of silica with the simultaneous chlorination of the silicon so formed. D.I.Mendeleyev (Bibl.4) prepared silicon tetrachloride by heating a mixture of silica, carbonized starch and coal in a current of chlorine to "white heat".

$$\text{SiO}_2 + 2\text{C} + 2\text{Cl}_2 \rightarrow \text{SiCl}_4 + 2\text{CO}$$

Budnikov and Shpilov (Bibl.5) synthesized silicon tetrachloride by the action of phosgene on silica in the presence of carbon black as a catalyst.

$$\text{SiO}_2 + 2\text{COCl}_2 \rightarrow \text{SiCl}_4 + 2\text{CO}_2$$

The optimum reaction temperature is 1000°C. The yield depends strongly on the degree of disperseness of the silica.

When precipitated silica gel is used, the yield could be brought up to 62% of theoretical.
In a number of works and patents (Bibl.6) various methods of preparing silicon tetrachloride have been proposed: heating carborundum in a current of chlorine at 1000 - 1200°C; passage of a mixture of sulfur polychloride and sulfur over incandescent briquettes of a mixture of silica (or silicates) with coal; treatment of silica with boron trichloride; passage of chlorine through a mixture of aluminosilicates and coal at high temperatures. The latter method deserves attention in view of the fact that two valuable products are obtained at the same time as a result of the reaction, silicon tetrachloride and aluminum chloride.

Silicon tetrachloride is a heavy mobile liquid. The product usually contains dissolved chlorine as an impurity. To remove it the silicon tetrachloride must be distilled over mercury. This method of purification was proposed by D.I. Mendeleyev (Bibl.4) as long ago as the middle of the last Century.

Some Physical Constants of Silicon Tetrachloride

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Gravity at 15°C</td>
<td>1.49276</td>
</tr>
<tr>
<td>Index of Refraction nD^20</td>
<td>1.41257</td>
</tr>
<tr>
<td>Melting Point °C</td>
<td></td>
</tr>
<tr>
<td>According to Stock</td>
<td>-67.7</td>
</tr>
<tr>
<td>According to Moissan</td>
<td>-89</td>
</tr>
<tr>
<td>Surface Tension at 18.9°C, dynes/cm</td>
<td>16.31</td>
</tr>
<tr>
<td>Capillary Constant at 15°C</td>
<td>2.797</td>
</tr>
<tr>
<td>Critical Temperature, °C</td>
<td>230</td>
</tr>
<tr>
<td>Specific Heat, cal/kg</td>
<td></td>
</tr>
<tr>
<td>Liquid</td>
<td>0.1904</td>
</tr>
<tr>
<td>Gaseous</td>
<td>0.1322</td>
</tr>
<tr>
<td>Trouton Constant</td>
<td>21.0</td>
</tr>
<tr>
<td>Dielectric Constant</td>
<td>2.4</td>
</tr>
<tr>
<td>Molecular Cohesion at 15°, cal/mol</td>
<td>712.3</td>
</tr>
<tr>
<td>Dissolved Chlorine at 20°C, % (by weight)</td>
<td>1</td>
</tr>
</tbody>
</table>
Fajans has investigated the electronic structure of silicon tetrachloride (Bibl.7).

**Hydrolysis of Silicon Tetrachloride and Condensation of Hydrolyzate**

The reaction of hydrolysis of silicon tetrachloride takes place almost instantaneously and very energetically. The heat of reaction of silicon tetrachloride with an excess of water is 69.3 kcal/mol. As a result of hydrolysis, HCl and the polymeric product of the condensation of orthosilicic acid [Si(OH)₄], silica gel, are formed.

The tendency of the initially formed hydroxyl derivatives of silicon to intermolecular condensation, forming complex molecules with siloxane bonds

\[
\begin{align*}
\text{Si-OH + H-O-Si} & \rightarrow \text{Si-O-Si} + \text{H₂O} \\
\end{align*}
\]

is the basis of the formation of the polysiloxanes and of the modern technology of polyorganosiloxanes.

The mechanism of the condensation of organodihydroxy silanes was investigated only toward the 1930’s.

The hypothesis that this process proceeds toward the formation of high-molecular inorganic hydroxyl derivatives of silicon was enunciated long ago. The first of such guesses was advanced by D.I. Mendeleev, who as early as the 1850’s came to the conclusion of the “polymeric nature of inorganic oxygen compounds of silicon” (Bibl.8). Even then, when scientists know nothing of the processes of formation of high-molecular compounds, Mendeleev was able to point out the fundamental direction of the process toward the formation of a high-molecular polysiloxane.

We cite Mendeleev’s own words:

Orthosilicic acid Si(OH)₄, formed on the action of water on silicon tetrachloride, “does not remain in that form, but loses part of its water with extraordinary ease” ..., the hydrate formed is not actually obtained with as high a water content as
corresponds to Si(OH)$_4$; "in the hydrates nSiO$_2$ . mH$_2$O, m becomes smaller and smaller than n.... This loss of water proceeds, in the natural hydrates, in perfect sequence, and, so to speak, imperceptibly, until n becomes incomparably greater than m".

The transition can be so gradual only with a considerable value of n, and therefore... "the structure of silica is polymeric, complex, instead of simple, as it is expressed by its empirical formula"... "it is necessary to explain the ability of (SiO$_2$)$_n$ to combine with (RO)$_{m-1}$, where n may be more than m and R = H$_2$.

To explain this the facts obtained in the study of organic substances, more specifically, originally with respect to glycol, have been very useful".

Mendeleyev gives an example of the intermolecular condensation of glycol into polyglycols by the following mechanism: HOC$_2$H$_4$OH + HOC$_2$H$_4$OH $\rightarrow$ HOC$_2$H$_4$OC$_2$H$_4$OH + H$_2$O, and writes the general formula of polyglycols as A$_n$ . H$_2$O, where A is the dehydrated residue of ethylene oxide [OC$_2$H$_4$].

In comparing the processes of formation of polyglycol and silica gel, Mendeleyev writes:

"The relation between the hydrate of silica and silica is the same.... To the normal hydrate of silicon Si(OH)$_4$ there must correspond several polyhydrates (SiO$_2$)$_n$ (H$_2$O)$_m$, where n may be very great".

From these quotations it will be rather clear that Mendeleyev imagined the dehydration of orthosilicic acid as a process of intermolecular condensation with the formation of high molecular polysiloxane. Such a view in the 1850's and 1860's was so new that it met neither support nor understanding among scientists from the 1860's to the 1890's. It was only in 1892 that Stock's paper (Bibl.8a) was published, in which the polymer (Cl$_2$SiO)$_n$ is considered as a polysiloxane, the author having reached this conclusion on its structure on the basis of Mendeleyev's views.

The condensation of the hydroxyl derivatives of silica into polysiloxanes is today an established fact. The condensation of the hydrolyzates of silicon tetra-
chloride proceeds at a considerably higher velocity than the condensation of the hydroxysilanes $R_n\text{Si(OH)}_{4-n}$, and leads to the formation of end products of more complex structure. These differences naturally operate to complicate materially the studies of the course of the reaction, and therefore the studies of the initial products of the hydrolysis of silicon tetrachloride and of the products of their condensation are all very recent (Bibl.9). The results of this work show that this process, with insufficient water, takes place by a mechanism analogous to that established by me in 1938 for the hydrolysis and condensation of the hydrolyzates of the substituted esters of orthosilicic acid. This mechanism is today generally accepted to explain the condensation of all hydroxyl-containing organic derivatives of silicon.

To explain the mechanism of the process and to obtain the maximum yields of the initial products of hydrolysis and condensation, the mildest conditions of conducting the hydrolysis reaction were selected.

The hydrolysis of an ethereal solution of silicon tetrachloride by aqueous ether at $-75^\circ$C leads to the formation of only small quantities of hexachlorodisiloxane $\text{Cl}_3\text{SiOSiCl}_3$. Polysiloxanes that can be distilled, and which form gels, are mainly formed, however.

By the action of ice ground to powder on an ethereal solution of $\text{SiCl}_4$, as much as 11% of hexachlorodisiloxane, together with other initial condensation products, could be isolated.

We now present the techniques of a few of the most successful experiments.

**Hydrolysis of silicon tetrachloride by ice.** A solution of 100 ml of silicon tetrachloride in 150 ml of ethyl ether is cooled to $-75^\circ$C, after which, with stirring, 6.4 g of ice ground to powder and cooled to $-75^\circ$C are gradually introduced into the $\text{SiCl}_4$ solution (ratio: 0.84 mol $\text{H}_2\text{O}$ to 2 mols $\text{SiCl}_4$). The introduction of the ice takes an hour, after which the reaction mass is held for an hour at $-75^\circ$C, and is then gradually brought up to room temperature. The reaction product is dis-
tilled at atmospheric pressure to $150^\circ$C and then in vacuo at a reduced pressure of 12 mm Hg. The fraction collected from several experiments are combined and redistilled. The following content of the initial products of hydrolysis was found in the reaction products:

<table>
<thead>
<tr>
<th>Boiling Point $^\circ$C</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexachlorodisiloxane Cl$_3$SiOSiCl$_3$</td>
<td>135</td>
</tr>
<tr>
<td>Octachlorodisiloxane Cl$_3$SiOSiCl$_2$OSiCl$_3$</td>
<td>184</td>
</tr>
<tr>
<td>Decachlorotetrasiloxane Cl$_3$SiO(SiCl$_2$O)$_2$SiCl$_3$</td>
<td>205</td>
</tr>
</tbody>
</table>

The method of hydrolysis by the action of hydrated inorganic salts on an ether solution of silicon tetrachloride proved considerably more convenient. In this case, even when the reaction is conducted at room temperature, the uncondensed initial product of hydrolysis, trichlorohydroxysilane Cl$_3$SiOH*, can be isolated.

The best results are obtained on reaction with nickel chloride hexahydrate NiCl$_2$·6H$_2$O.

**Hydrolysis of silicon tetrachloride in presence of hydrated salts.** Into a solution of 100 ml of SiCl$_4$ in 50 ml of ether at room temperature, without stirring, 19.7 g of copper sulfate CuSO$_4$ · 5H$_2$O is introduced (molar ratio SiCl$_4$ : H$_2$O = 2 : 0.93); the mixture is allowed to stand for 8 days and is then distilled under atmospheric pressure. The fraction boiling at 100 - 130$^\circ$C (amounting to 5.2%) and mainly consisting of trichlorohydroxysilane (pp. 110 - 120$^\circ$C) is collected.

To a solution of 150 ml of SiCl$_4$ and 50 ml of ether at room temperature, 24 g of NiCl$_2$ · 6H$_2$O is added under stirring (molar ratio SiCl$_4$ : H$_2$O = 2 : 0.12). After distillation of the reaction product, the fraction boiling at 100 - 130$^\circ$C is collected, and yields on redistillation 3 g of trichlorohydroxysilane (boiling point

*Trichlorohydroxysiloxane had previously been obtained by photochemical oxidation of trichlorosilane (Bibl.10).
Trichlorohydroxysilane condenses spontaneously; thus, after standing at room temperature for 4 days, about 83% of the original quantity passes over up to 130°C, while after 14 days, only 27% passes over. On heating trichlorohydroxysilane with $P_2Cl_5$, it is quantitatively converted to hexachlorodisiloxane (boiling point 135°C).

On the action of $NiCl_2 \cdot 6H_2O$ on a solution of $SiCl_4$ at $0°C$ (molar ratio $SiCl_4 : H_2O = 2 : 1$ to $2 : 2$) in a series of experiments, a mixture containing the following quantities of condensed hydrolyzates was obtained.

<table>
<thead>
<tr>
<th>Boiling Point</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexachlorodisiloxane $Cl_3SiOSiCl_3$</td>
<td>135</td>
</tr>
<tr>
<td>Octachlorotrisiloxane $Cl_3SiOSiCl_2OSiCl_3$</td>
<td>184</td>
</tr>
<tr>
<td>Decachlorotetrasiloxane $Cl_3Si(OSiCl_2)_2OSiCl_3$</td>
<td>205</td>
</tr>
<tr>
<td>Pentachlorohydroxydisiloxane $Cl_3SiOSiCl_2OH$</td>
<td>175-176</td>
</tr>
</tbody>
</table>

The reaction of an ether solution of silicon tetrachloride with cobalt and nickel hydroxides, dried at $170 - 180°C$, and with sodium carbonate decahydrate $Na_2CO_3 \cdot 10H_2O$ proceeds similarly. In these cases the yield of trichlorohydroxysilane and pentahydroxysilane is somewhat increased.

The linear chloropolysiloxanes of higher molecular weight have very recently been prepared by the following technique:

**Hydrolysis of silicon tetrachloride in ether solution at low temperature.** An ether solution of $SiCl_4$ is cooled to $-78°C$ and placed in a burette, and is then rapidly poured, under vigorously stirring, into a mixture of water and ether. On contact with the cold solution, all the water immediately freezes, and the hydrolysis is probably effected by the ice. The reaction product is then gradually warmed to room temperature, after which it is a transparent colorless liquid completely or almost completely free of a silica gel precipitate. The hexachlorodisiloxane and the unreacted $SiCl_4$ are distilled off under atmospheric pressure, and the residue is carefully reactified under a reduced pressure of 15 mm. In a series of experiments
run at molar ratio $\text{SiCl}_4$ from 2 to 10 and with 0.5 to 6 mols of ether to 1 mol of $\text{H}_2\text{O}$.

$\text{SiCl}_4$, a mixture was obtained from which the following linear polychlorosiloxanes, together with the unreacted $\text{SiCl}_4$, were separated and investigated.

<table>
<thead>
<tr>
<th>Boiling Point $^\circ\text{C}$</th>
<th>Yield, % of Weight of Polychlorosilanes Separated</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cl}_3\text{SiOSiCl}_3$ . . . . . . .</td>
<td>134 (760 mm) 50.7</td>
</tr>
<tr>
<td>$\text{Cl}_3\text{Si(OSiCl}_2)\text{OSiCl}_3$ . .</td>
<td>80.5 (15 mm) 19.6</td>
</tr>
<tr>
<td>$\text{Cl}_3\text{Si(OSiCl}_2)\text{_2OSiCl}_3$ . .</td>
<td>114.7 (15 mm) 12.5</td>
</tr>
<tr>
<td>$\text{Cl}_3\text{Si(OSiCl}_2)\text{_3OSiCl}_3$ . .</td>
<td>140 (15 mm) 7.8</td>
</tr>
<tr>
<td>$\text{Cl}_3\text{Si(OSiCl}_2)\text{_4OSiCl}_3$ . .</td>
<td>166-167 (15 mm) 5.5</td>
</tr>
<tr>
<td>$\text{Cl}_3\text{Si(OSiCl}_2)\text{_5OSiCl}_3$ . .</td>
<td>187-188 (15 mm) 3.9</td>
</tr>
</tbody>
</table>

The residue (175 g of substance), consists of high boiling products with boiling point over 190° (at 15 mm).

No cyclical condensation products were found in the reaction mixture.

The solvent plays a very important role in the establishment of the mildest conditions of hydrolysis. Various investigators have noted that only the use of ethyl ether or dioxane makes it possible to obtain and isolate a sufficient quantity of the intermediate reaction products. To elucidate the role of the solvent in establishing mild conditions of hydrolysis at low temperatures, the influence of the quantity of solvents used on the course of hydrolysis were studied.

The yield of hexachlorodisiloxane was used as the criterion for evaluating the results of the experiment. This substance is a product of hydrolysis which can be more easily isolated in the pure state than the other products (in addition, its content in the mixtures can be rather accurately calculated from the data of the elementary analysis).

The theoretical yield of hexachlorodisiloxane may be calculated on the basis of
the statistical equation of Stock and Meyer (Bibl.12). This equation, which enables us to calculate the distribution of molecules of definite sizes in polydisperse mixtures, is based on the assumptions that only linear molecules are formed and that all functional groups have the same activity, which is obviously sufficiently correct for the system under consideration.

The application of the Stock-Meyer equation makes it possible to deduce the following relation:

\[
\frac{[\text{SiCl}_4]}{[\text{H}_2\text{O}]} = 1 - \frac{1}{2 \cdot \frac{[\text{SiCl}_4]}{[\text{H}_2\text{O}]}^{1/2}}
\]

whence, at a given molar ratio \( \frac{[\text{SiCl}_4]}{[\text{H}_2\text{O}]} \), the concentration of hexachlorodisiloxane can always be more or less accurately calculated. In practice, the yield of hexachlorodisiloxane is usually found to be lower than the calculated yield, the percentage yield strongly varying with the relative proportion of ethyl ether. The lowering of the percentage yield is found to be a regular function of the molar ratio \( \frac{[(\text{C}_2\text{H}_5)_2\text{O}]}{[\text{H}_2\text{O}]} \) (Fig.2).

It has not been possible to establish the relation between the yield and the molar ratio \( \frac{[\text{SiCl}_4]}{[(\text{C}_2\text{H}_5)_2\text{O}]} \), since the results are entirely different, and, apparently, random. This gives us reason to suppose that the presence of ether makes the conditions of hydrolysis milder, not as a result of some reaction with silicon tetrachloride, but owing to a reaction with water. This hypothesis is supported by the fact that silicon tetrachloride forms no coordination compounds with simple ethers (Bibl.13). The results of the experiments in the elucidation of the influence of ethyl ether on the process of hydrolysis may be explained on the basis of the
following hypothesis.

The oxonium compound:

$$(\text{C}_2\text{H}_5\text{O})_2\text{OH} + \text{HCl} \rightarrow (\text{C}_2\text{H}_5\text{O})_2\text{HCl}$$

formed by ether and HCl is capable of reaction with water at a low temperature:

$$(\text{C}_2\text{H}_5\text{O})_2\text{HCl} + \text{H}_2\text{O} = (\text{C}_2\text{H}_5\text{O})_2\text{HCl} \cdot \text{H}_2\text{O}$$

The structure of the unstable compound so obtained may be represented on the basis of the following mechanism:

The compound so obtained has one active hydrogen atom which reacts with the chlorine atom in SiCl$_4$ more easily than the hydrogen atom of water does:

$$(\text{C}_2\text{H}_5\text{O})_2\text{HCl} \cdot \text{H}_2\text{O} + \text{SiCl}_4 \rightarrow \text{ClSiCl}_3 \cdot \text{Cl}_2\text{SiOH} \cdot (\text{C}_2\text{H}_5\text{O})_2\text{HCl} \cdot \text{HCl}$$

or

$$\text{ClSiCl}_3 \cdot \text{Cl}_2\text{SiOH} \cdot (\text{C}_2\text{H}_5\text{O})_2\text{HCl} \cdot \text{HCl}$$

The decrease in the yield of hexachlorodisiloxane with increasing number of mols of ether (by comparison with the number of mols of water) may be explained by
the formation of a compound with two active centers:

\[(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{H}_2\text{O} \cdot \text{HCl} + (\text{C}_2\text{H}_5)_2\text{O} = (\text{C}_2\text{H}_5)_2\text{O} \cdot \text{H}_2\text{O} \cdot (\text{C}_2\text{H}_5)_2\text{O} \cdot \text{HCl}\]

or

\[\begin{align*}
\text{H}_2\text{C}_2\text{O} & \quad \text{H} \quad \text{O} \quad \text{H} \quad \text{H} \quad \text{Cl}^- \\
\text{H}_2\text{C}_2\text{O} & \quad \text{H} \quad \text{H} \quad \text{Cl}^- \quad \text{O} \quad (\text{C}_2\text{H}_5)_2\text{O} \\
\text{H}_2\text{C}_2\text{O} & \quad \text{H} \quad \text{H} \quad \text{Cl}^- \quad \text{O} \quad (\text{C}_2\text{H}_5)_2\text{O}
\end{align*}\]

Such a compound may play the role of a bifunctional compound encouraging the formation of high-polymer products in quantities larger than the statistical, and, consequently, reducing the practical yield of hexachlorodisiloxane below the calculated level.

Dioxane, probably, reacts according to an analogous mechanism. Other solvents do not enter into reaction like those just discussed, and thus their use does not encourage the softening of the conditions of hydrolysis to so significant an extent.

The hydrogen chloride formed during hydrolysis apparently catalyzes the condensation process. This is confirmed by the fact that when the hydrolysis is run in the presence of neutralizing substances (hydroxides of metals or sodium) a large quantity of hydroxysilanes are formed, while in the case of the saturation of the solution by HCl before hydrolysis, the process leads to the formation of insoluble polymers.

It must be noted that when an insufficient quantity of water acts under mild conditions on a solution of SiCl₄, a mixture consisting of linear polychlorosiloxanes Cl₂Si(OSiCl₃)₂OSiCl₄, and lower hydroxy derivatives containing not more than one hydroxyl group to the silicon atom is formed; cyclic condensation products have not been found. This gives us reason to consider that the process of hydrolysis of SiCl₄ proceeds according to a mechanism analogous to that of the hydrolysis of alkylchlorosilanes and the substituted ethers of orthosilicic acids.

In the general form, the hydrolysis of silicon tetrachloride may be represented
by the following diagram:

\[ 
\begin{align*}
\text{SiCl}_4 & \rightarrow \text{Cl}_2\text{SiOH} \rightarrow \text{Cl}_2\text{Si(OH)} \rightarrow \text{ClSi(OH)} \rightarrow \text{Si(OH)} \rightarrow \text{Si(OH)} \rightarrow \text{Si(OH)} \\
\text{Cl}_2\text{SiOSiCl}_3 & \rightarrow \text{Cl}_2\text{SiOH} \rightarrow \text{ClSi(OH)} \rightarrow \text{Si(OH)} \rightarrow \text{Si(OH)} \rightarrow \text{Si(OH)} \\
\text{H}_2\text{SiCl}_2 & \rightarrow \text{Si(OH)} \rightarrow \text{Si(OH)} \rightarrow \text{Si(OH)} \rightarrow \text{Si(OH)} \rightarrow \text{Si(OH)} \\
\text{H}_2\text{SiOCl} & \rightarrow \text{Si(OH)} \rightarrow \text{Si(OH)} \rightarrow \text{Si(OH)} \rightarrow \text{Si(OH)} \rightarrow \text{Si(OH)} \\
\text{H}_2\text{SiO}_2 & \rightarrow \text{Si(OH)} \rightarrow \text{Si(OH)} \rightarrow \text{Si(OH)} \rightarrow \text{Si(OH)} \rightarrow \text{Si(OH)} \\
\text{H}_2\text{SiO}_3 & \rightarrow \text{Si(OH)} \rightarrow \text{Si(OH)} \rightarrow \text{Si(OH)} \rightarrow \text{Si(OH)} \rightarrow \text{Si(OH)} \\
\text{H}_2\text{SiO}_4 & \rightarrow \text{Si(OH)} \rightarrow \text{Si(OH)} \rightarrow \text{Si(OH)} \rightarrow \text{Si(OH)} \rightarrow \text{Si(OH)} \\
\end{align*} 
\]

The arrows pointing from left to right schematically denote the reaction of hydrolysis at the Si-Cl bond:

\[ 
\begin{align*}
\text{Si-Cl} + \text{H}_2\text{O} & \rightarrow \text{Si-OH} + \text{HCl} \\
\end{align*} 
\]

The vertical arrows indicate the processes of condensation:

\[ 
\begin{align*}
\text{Si-OH} + \text{H}_2\text{O} & \rightarrow \text{Si-OH} + \text{H}_2\text{O} \\
\end{align*} 
\]

The combination of these two processes leads to the formation of the most varied polychlorosiloxanes, polyoxychlorosiloxanes, polycyoxysiloxanes, and, as the end product, high-molecular polysiloxane \((\text{SiO}_2)_x\).

The ratio between the velocities of the processes of hydrolysis and condensation, and consequently the formation of these or those intermediate products of hydrolysis, depends on a number of factors: the ratio between the amounts of silicon tetrachloride and water, the acidity of the medium, the temperature, the rate of stirring, the presence of solvents and of salts that bind water, etc. It is not at the present time possible to evaluate completely the influence of all these factors.

In running a hydrolysis with insufficient water, the above discussed reaction
of SiCl₄ proceeds with the formation of the following intermediates:

\[
\begin{align*}
\text{SiCl}_4 + \text{H}_2\text{O} & = \text{Cl}_2\text{Si(\text{OH})} + \text{HCl} \\
\text{Cl}_3\text{Si(\text{OH})} + \text{HOSiCl}_3 & = \text{Cl}_4\text{SiOSiCl}_3 + \text{H}_2\text{O} \\
\text{Cl}_4\text{SiOSiCl}_3 + \text{H}_2\text{O} & = \text{Cl}_4\text{SiOSiCl}_2\text{OH} + \text{HCl} \\
\text{Cl}_4\text{SiOSiCl}_2\text{OH} + \text{Cl}_2\text{Si(OH)} & = \text{Cl}_4\text{SiOSiCl}_2\text{OSiCl}_3 + \text{H}_2\text{O} \quad \text{etc.}
\end{align*}
\]

with the formation of linear or branched polychlorosiloxanes. It should be borne in mind, however, that the reaction mixture was separated at a high temperature (100 - 200°C), without using a high vacuum.

It is entirely probable that, during the course of the reaction, a large quantity of hydroxyl-containing compounds are formed, for example (OH)Cl₂Si-O-SiCl₂(OH), which are condensed at high temperatures, as a result of which siloxanes are the main products formed.

The reaction between silicon tetrachloride and a considerable excess of water in a weakly acid medium proceeds in an entirely different way. This reaction has been investigated in detail by Willstatter (Bibl.14) who, in order to prepare solutions of orthosilicic acid, studied in detail the hydrolysis of silicon tetrachloride and of the subsequent condensation of the hydrolysis products. He established that this process can be represented in the form of the reactions:

\[
\begin{align*}
\text{SiCl}_4 + \text{H}_2\text{O} & = \text{Cl}_2\text{Si(\text{OH})} + \text{HCl} \\
\text{Cl}_3\text{Si(\text{OH})}_2 + \text{H}_2\text{O} & = \text{Cl}_4\text{Si(\text{OH})}_2 + \text{HCl} \\
\text{Cl}_4\text{Si(\text{OH})}_2 + \text{H}_2\text{O} & = \text{Cl}_4\text{Si(\text{OH})}_3 + \text{HCl} \\
\text{Cl}_4\text{Si(\text{OH})}_3 + \text{H}_2\text{O} & = \text{Cl}_4\text{Si(\text{OH})}_4 + \text{HCl} \\
(\text{HO})_2\text{Si(\text{OH})}_2 + \text{HOSi(OH)}_2 & = (\text{HO})_3\text{SiOSi(OH)}_2 + \text{H}_2\text{O} \\
(\text{HO})_2\text{SiOSi(OH)}_2 + \text{HOSi(OH)}_2 & = (\text{HO})_3\text{SiOSi(OH)}_3 + \text{H}_2\text{O} \quad \text{etc.}
\end{align*}
\]

As a result of these reactions linear and branched hydroxylpolysiloxanes of increasing molecular weight are formed.
The basic factor affecting the velocity of condensation of hydroxysilanes in dilute aqueous solutions, according to Willstatter's data, is the acidity of the medium (the concentration of HCl). If the pH of the solution is held within the limits of 2 - 4, it is apparently possible to obtain dilute solutions of orthosilicic acid even in the absence of a solvent, and at a relatively high reaction temperature (0°C). A method of preparing dilute solutions of orthosilicic acid is given below.

Preparation of dilute solutions of orthosilicic acid. A thoroughly dried inert gas or air is bubbled through a weighed portion of silicon tetrachloride (12.5 g), placed in an evaporating flask, heated in a water bath (at 60 - 65°C). The vapor of SiCl₄, entrained by the current of gas, is passed over a layer of a vigorously stirred mixture of water and ice. If the process is performed with the object of obtaining a polymeric product, without neutralization, then the vapor-gas mixture, to avoid clogging the capillary, must be introduced through a mercury seal. To obtain a solution of orthosilicic acid, the vapor is passed, through a capillary, directly into water. The process is conducted, neutralizing the HCl given off by wet silver oxide, which allows holding the pH of the solution within the optimum range, thereby preventing gelation. The mixture of gas and SiCl₄ vapor is introduced under a layer of vigorously stirred mixture of water and ice (750 g in all). The glass vessel is cooled by brine from outside to hold the temperature at 0°C until the end of the experiment. Simultaneously with the beginning of the passage of the vapor into the cylinder, a paste of wet silver oxide obtained by precipitation from 50 g of silver nitrate is introduced. The process of introducing the SiCl₄ takes 20 - 30 minutes; at the end of the reaction the brown color of silver hydroxide disappears, since its quantity is insufficient for complete neutralization of the HCl. The acidity is then strictly checked and adjusted by adding silver oxide paste to reaction mixture. Toward the end of the experiments the concentration of HCl is adjusted to within the range from 0.01 to 0.001 N. The reaction product is subjected to suction on a Nutch
filter through a layer of activated charcoal. The completely transparent filtrate (800 ml) contain 3.67 - 3.78 mg of SiO₂ in 10 ml of solution, which corresponds to a yield of 80% of the theoretical yield of the hydrolysis product.

Owing to the presence of orthosilicic acid, the pH of the solution exceeds the value corresponding to the concentration of HCl. Thus a solution with 0.01 N HCl has a pH = 2.5 instead of 2. The cryoscopic determination of the molecular weight of the hydrolysis product in this solution gives the value of 75. In the most successful experiment, the reaction product was characterized by the following data:

- Concentration of HCl: \( \frac{1}{700} \) N
- pH of Solution: 3.4
- SiO₂ Content: 0.5%
- Molecular Weight (in Terms of SiO₂): 62

Thus the possibility of preparing orthosilicic acid in dilute aqueous weakly acid solution must be considered to have been demonstrated.

The solutions prepared by this method contain an insignificant quantity of HCl (1 mol HCl to 10 - 100 gram atoms of silicon). Moreover, in the author’s opinion, an insignificant number of chlorine atoms remain bound to the silicon (probably in the form of ClSi(OH)₃, since on neutralization to the faint yellowing of a solution containing methyl red, the red color of the solution is restored again after 15 - 20 sec, this phenomenon being repeated until the complete neutralization of all the chlorine.

Willstatter studied in detail the process of condensation at room temperature of dilute solutions of orthosilicic acid at various pH values. The results of the study (Fig.3) indicate the relative stability of the solutions at HCl concentrations from 0.01 N to 0.001 N. Thus, for example the molecular weight of the lowest molecular preparation rises in 4½ hours after the experiment from 62 to only 67, while to accomplish the first stage of the condensation by the formula.
about 2½ days are necessary. It is interesting to note that for a given solvent (acidity of HCl \( \frac{1}{700} \) N) the curve of variation of molecular weight with time (curve 4) has an inflection at the point approximately corresponding to the formation of the initial condensation products by the reaction given above, which may point to the relatively low velocity of condensation with the second hydroxyl group by comparison with the velocity of condensation with the first OH group. At other values of the acidity, this phenomenon is not observed, and thus the product of condensation here is a polydisperse mixture of hydroxypolsiloxanes.

According to the author's data, the acidity has considerably greater effect on the stability of monomeric orthosilicic acid than, for example, on the stability of the initial condensation product \((\text{HO})_3\text{SiOSi(OH)}_3\) which can be maintained for a certain length of time in 0.5 N HCl solution. Dilute aqueous solutions of orthosilicic acid and the initial products of its condensation in a weakly alkaline medium (ammonia solution) and in a solution of ammonium chloride were found to be the least stable.

The rate of condensation of orthosilicic acid in dilute weakly acid solutions is considerably slowed after reaching a degree of condensation equal to 6.

As for the processes of further
condensation, it is not possible today to give an exact picture of them. The diagram on page 86 merely shows that the process of condensation leads to the formation of cross-linked and three-dimensional structures and, ultimately, to high-molecular three-dimensional polysiloxane (SiO₂)ₓ.

The two examples of the conduct of the hydrolysis reaction discussed above, the action of a minimum quantity of water under mild conditions, and in dilute aqueous solutions using neutralization, both constitute stepwise processes which proceed almost according to the theoretical mechanism. In practice, when the hydrolysis reaction is run either with silicon tetrachloride or with esters of orthosilicic acid and alkyl-(aryl)-chlorosilanes, the process may proceed in the most varied directions. The compounds (intermediate products) so formed may contain various numbers of hydroxyl groups or chlorine atoms, may have various siloxane chain lengths, may possess a linear, cyclic, or three-dimensional structure, etc. The formation of these or those intermediate products depends on the ratio between the reaction velocities of hydrolysis and condensation. The end product of hydrolysis, silica gel, however, is in all cases a high molecular hydroxypolysiloxane.

According to Willstatter (Bibl.14), the gel obtained by means of the hydrolysis of silicon tetrachloride, after centrifuging, contains about 15% of water bound to the silicon atoms in the form of hydroxyl groups or adsorbed by the active surface of the gel. On the spontaneous condensation of the gel under water, equilibrium is established in about three months, with the gel containing 11.45% of bound water. The adsorptive properties of the gel vary considerably according to the method of hydrolysis; thus, for example, the gel obtained by hydrolysis in alkaline medium contains 21.8% of bound water in its initial state.

The main factor determining the number of free hydroxyl groups in the end reaction product, when the hydrolysis is run under ordinary conditions, is the reaction temperature. The compounds obtained on the reaction of silicon tetrachloride with water at an elevated temperature contains a smaller number of free OH groups;
but if the hydrolysis is conducted in the vapor phase at a temperature of the order of 500°C, the reaction product is crystalline silicon dioxide.

\[ \text{SiCl}_4 + 2\text{H}_2\text{O} \rightarrow (\text{SiO}_2) \cdot 4\text{HCl} \]

The silica gel obtained under ordinary conditions gradually undergoes condensation in air; the molecular weight increases, and the number of free OH groups as well as the quantity of adsorbed water decreases; the structure of such a gel has been studied by washing away the water with acetone (Bibl.15). The authors reached the conclusion that hydrated silicas, for example 2\(\text{SiO}_2 \cdot \text{H}_2\text{O}\), could be prepared. In view of the fact that the products so formed are a polydisperse mixture of high-molecular compounds, we consider it very improbable that molecules could be formed with so simple a ratio between the number of silicon atoms and the number of free hydroxyl groups or the quantity of adsorbed water.

The spontaneous condensation of silica gels in air leads to a considerable decrease in the quantity of bound water (Bibl.16); at room temperature a product corresponding to the empirical formula \(10\text{SiO}_2 \cdot \text{H}_2\text{O}\) may be obtained. The remaining hydroxyl groups are bound very firmly, and are not removed even at a temperature of 300 - 400°C. The process of condensation is completed only at 1000°C. In this case the silica gel passes over into the crystalline state and completely loses its adsorptive properties.

The reaction between silicon tetrachloride and water cannot be represented by any single chemical formula. In considering the mechanism of the process, the whole group of possible reaction must be borne in mind. For simplification it is advisable to represent the aggregate of the processes of hydrolysis and condensation of the hydrolysis products by the following arbitrary system:

\[ \text{SiCl}_4 + 2\text{H}_2\text{O} \rightarrow [\text{SiOH}_2] + 4\text{HCl} \]

But such a formula indicates only the principal direction of the reaction toward the
hydrolysis of all four chlorine atoms and the formation of silica gel. It must be
borne in mind that, in reality, as shown above, the process takes a considerably
more complex course.

**Reaction of Silicon Tetrachloride with Various Organic and Inorganic Compounds**

Silicon tetrachloride, as a acid chloride, readily reacts with compounds con-
taining a free hydroxyl group. The reaction of SiCl₄ with organic compounds, de-
pending on the number of OH groups, their mobility, and the molecular structure of
the organic compound, may proceed in two entirely different directions:

1. Replacement of chlorine by an OH group:

\[
\text{Si-Cl + HO-\text{R} \rightarrow Si-OH + Cl-\text{R}}
\]

In this case the molecule of the organic compound may be dehydrated:

\[
\text{Si-Cl + HO-\text{R} \rightarrow Si-OH + HCl + \text{R}}
\]

Similar transformations may take place not only with compounds containing OH groups
but also with other oxygen-containing compounds.

2. Formation of molecules with an ether bond:

\[
\text{Si-Cl + HO-\text{R} \rightarrow Si-\text{O}-\text{R} + Cl-}
\]

In this way the reactions of the first type lead to the ultimate formation of silica
gel and a modified organic derivative. By reactions of the second type organosili-
con ethers or mixed organosilicon anhydrides may be obtained. Let us consider these
two types of reactions.
Reactions Leading to the Formation of Silica Gel

Organic acids, on reaction with an excess of silicon tetrachloride form, under severe conditions, the corresponding acid chlorides and silica gel (Bibl.17):

\[
\text{SiCl}_4 + 4\text{RCOOH} \rightarrow [\text{Si(OH)}_4] + 4\text{RCOCl}
\]

Andrianov and Dolgopolov (Bibl.18), on the basis of a reaction of this type, have developed an industrial method of producing benzoyl chloride from \(\text{SiCl}_4\) and benzoic acid. The yield of benzoyl chloride is 95% of theoretical. Owing to the inexpensiveness and ready availability of \(\text{SiCl}_4\) (by comparison with such chlorinating agents as \(\text{PCl}_5\) or \(\text{PCl}_3\)) the synthesis of organic acid chlorides by this method is of considerable interest.

Tertiary aromatic alcohol reacts with \(\text{SiCl}_4\) by an analogous mechanism (Bibl.19):

\[
\text{SiCl}_4 + 4\text{C}_6\text{H}_5\text{COH} \rightarrow [\text{Si(OH)}_4] + 4\text{C}_6\text{H}_5\text{COCl}
\]

When isopropyl alcohol acts on \(\text{SiCl}_4\), silica gel, propylene and isopropyl chloride are formed (Bibl.20). Two parallel reactions obviously take place:

\[
\begin{align*}
\text{SiCl}_4 + 4\text{CH}_3\text{C(OH)}\text{CHOH} & \rightarrow [\text{Si(OH)}_4] + 4\text{CH}_3\text{C(OH)}\text{CHCl} \quad (1) \\
\text{SiCl}_4 + 4\text{CH}_3\text{C(OH)}\text{CHOH} & \rightarrow [\text{Si(OH)}_4] + 4\text{CH}_3\text{C(OH)}\text{CH}_2\text{C} + 4\text{HCl} \quad (2)
\end{align*}
\]

When acetone reacts with \(\text{SiCl}_4\), silica gel and a number of compounds from which mesityl oxide can be obtained, are formed (Bibl.21):

\[
\text{SiCl}_4 + 8\text{C}_3\text{H}_5\text{CO} \rightarrow [\text{Si(OH)}_4] + 4\text{C}_6\text{H}_5\text{COCH} = \text{C(CH}_3)_3 + 4\text{HCl}
\]
Other aldehydes and ketones react similarly.

**Reactions Leading to the Formation of Esters of Orthosilicic Acid**

The preparation of esters of orthosilicic acid by the reaction of SiCl₄ with monohydric alcohols and phenols by the reaction

\[ \text{SiCl}_4 + 4\text{ROH} \rightarrow \text{Si(OR)}_4 + 4\text{HCl} \]

is one of the processes that has been best studied and most used in practice.

The reaction of SiCl₄ with ethyl alcohol was first observed by Abelman (Bibl.22), but the structure of the products obtained was elucidated only in the 1850's by Mendeleev (Bibl.4, 23). The velocity of reaction depends in the first place on the activity of the alcohol or phenol. Methanol reacts at room temperature, at a velocity close to the velocities of inorganic reactions, and the replacement of chlorine atoms by methoxy groups proceeds to completion. Under the condition of removal of the HCl by blowing dry air through the product, the process can be conducted even at -10°C (Bibl.24). Kalinin (Bibl.25) found that when a solvent is used the reaction proceeds better, and the yield of tetramethoxysilane is 73% of theoretical. Ethyl alcohol reacts somewhat less energetically. The ethyl, isobutyl, allyl, benzyl and cyclohexyl esters of orthosilicic acid were prepared (Bibl.26) by pouring SiCl₄ into a 10% excess of the corresponding alcohol, heating the mixture on an oil bath until the evolution of HCl stopped, and then neutralizing the reaction product with sodium alcoholate. By a different method (Bibl.26) (in the cold, removing the HCl with a current of dry air, the ethyl, butyl, allyl, heptyl and octyl esters of orthosilicic acid were prepared.

The reaction of SiCl₄ with phenols (Bibl.27) is considerably less vigorous than even with such alcohols as octyl. Thus, for instance, SiCl₄ and phenol do not react for 1 - 2 hours; and this reaction can be completed only by heating the mixture to 250°C.

The reaction of SiCl₄ with insufficient alcohol or phenol leads to the forma-
tion of chloro esters:

\[
\text{SiCl}_4 + \text{ROH} = \text{Cl}_2\text{Si(OR)} + \text{HCl}
\]
\[
\text{Cl}_2\text{Si(OR)} + \text{ROH} = \text{Cl}_2\text{Si(OR)}_2 + \text{HCl}
\]
\[
\text{Cl}_2\text{Si(OR)}_2 + \text{ROH} = \text{Cl}_2\text{Si(OR)}_3 + \text{HCl}
\]

The reaction with the lower aliphatic alcohols is very energetic. As found by Kalinin (Bibl.25), the yield of chloroesters may be considerably increased by the use of an inert solvent, making the conditions of reaction milder; thus, in the presence of benzene as a solvent, butoxychlorosilanes were obtained (Bibl.28).

Allyloxychlorosilanes (Bibl.24) have been prepared in relatively high yield without using solvents.

The use of an organic base to neutralize the HCl liberated encourages the more quiet course of the reaction, but the isolation of the reaction product is made more difficult by the formation of hydrochlorides. When pyridine was used for neutralization, a number of halo-esters of tert-butyl and tert-amyl alcohols were prepared in the absence of a solvent (Bibl.29). The high boiling alcohols and phenols, which react with SiCl₄ less actively than the lower aliphatic alcohols, form mono- and dialkoxy chlorosilanes in good yield both with and without solvents. The process is completed after a short heating of the mixture on the water bath. Vol'nov (Bibl.30) prepared hexoxytrichlorosilane (yield 72%), dihexoxydichlorosilane (yield 41.6%), octoxytrichlorosilane (yield 60%), and a mixture of dioctydichlorosilane and trioctyoxychlorosilane (yields 28 and 22%) by this method. The reaction with dodecyl alcohol in a petroleum ether medium takes a similar course and leads to the formation of mono-, di-, and tridodecyloxychlorosilanes (Bibl.31).

Vol'nov and Mishelevich (Bibl.32), using ethyl ether as a solvent, prepared a number of chloro-esters of thymol, carvacrol and guiacol.

Other hydroxyl-containing organic compounds react similarly to simple aliphatic alcohol and phenols. Vol'nov (Bibl.33), investigating the reaction of SiCl₄ with
dihalohydrines of glycerine, obtained both the ester of orthosilicic acid:

\[
4\text{C}_2\text{H}_4\text{CHOH} + \text{SiCl}_4 = 4\text{HOCH}_2\text{Cl} + 4\text{HCl}
\]

and the di- and trihalo-esters:

\[
\begin{align*}
\text{CH}_2\text{BrCHBrCH}_2\text{OH} + \text{SiCl}_4 & = \text{Cl}_2\text{SiOC}_2\text{H}_4\text{CHBrCH}_2\text{Br} + 4\text{HCl} \\
\text{Cl}_2\text{SiOC}_2\text{H}_4\text{CHBrCH}_2\text{Br} + \text{CH}_2\text{BrCHBrCH}_2\text{OH} & = \text{Cl}_2\text{Si(OCH}_2\text{CHBrCH}_2\text{Br)}_2 + 4\text{HCl}
\end{align*}
\]

When the monomethyl or monoethyl esters of glycol act on \(\text{SiCl}_4\), even when an excess of such esters is used, the monochloro-ester is formed (Bibl.34):

\[
3\text{ROCH}_2\text{CH}_2\text{OH} + \text{SiCl}_4 = \text{Cl}_2\text{Si(OCH}_2\text{CH}_2\text{OR)}_2 + 3\text{HCl}
\]

On prolonged heating of the monomethyl ester of glycol with \(\text{SiCl}_4\) to complete removal of the HCl (Bibl.35), the full ester of orthosilicic acid can be obtained.

Ethylene oxide (Bibl.36) reacts with \(\text{SiCl}_4\) without forming HCl:

\[
\text{SiCl}_4 + 4\text{CH}_2\text{C}_2\text{H}_4\text{O} = \text{Si(OCH}_2\text{CH}_2\text{Cl)}_4
\]

The reaction is completed below 100°C. The yield of tetra-\(\beta\)-chloroethoxysilane is 73% of theoretical.

Compounds containing two OH groups react differently, depending on the mobility of the OH groups and the distances between them. Dolgov and Vol'nov (Bibl.37), studying the reaction of \(\text{SiCl}_4\) with dihydric phenols, found that hydroquinone and resorcinol react with two molecules of \(\text{SiCl}_4\), in the presence of an excess of \(\text{SiCl}_4\):

\[
2\text{SiCl}_4 + \text{C}_6\text{H}_4(\text{OH)}_2 \rightarrow \text{Cl}_2\text{SiOC}_6\text{H}_4\text{OSiCl}_3 + 2\text{vCl}
\]

while pyrocatechol reacts with only one molecule:
Ethylene glycol reacts somewhat differently (Bibl.38).

The first of the OH groups is replaced by chlorine:

\[
\text{SiCl}_4 + 4\text{HOCH}_2\text{OH} \rightarrow \text{[Si(OH)]}_4 + 4\text{ClH}_2\text{OH}
\]

The second OH group reacts with SiCl\(_4\) to form an ester:

\[
4\text{ClH}_2\text{OH} + \text{SiCl}_4 \rightarrow \text{Si(OCl)}_4 + 4\text{HCl}
\]

A precipitate was separated from the reaction mixture, and the author assigned the formula HOO\text{SiOC}_2\text{H}_4\text{OSiOOH} to it. At the present time the formation of such compounds is considered improbable. From our point of view there are more grounds for postulating that in this reaction a high molecular hydroxypolysiloxane is formed, a considerable part of whose OH groups are etherized by the unreacted ethylene glycol.

It is most probable of all that alongside of the substitution of an OH group of ethylene glycol by chlorine

\[
\text{Cl} \\
\text{Cl-Si-Cl + HOCH}_2\text{OH} \rightarrow \text{Cl-Si-OH} + \text{ClH}_2\text{OH}
\]

a condensation reaction also takes place; here halodisiloxanes would be formed:

\[
\text{Cl} \\
\text{Cl-Si-Cl + HO-Cl-Si-Cl} \rightarrow \text{Cl-Si-O-Si-Cl} + \text{H}_2\text{O}
\]

and a partial esterification of the substances formed would take place.
The water formed during the process of condensation causes hydrolysis followed by the formation of hydroxypolysiloxane, containing the ether groups which are more difficult to hydrolyze than the chlorine attached to the silicon atom:

\[
\begin{align*}
\text{Cl-Si-O-Si-Cl} + \text{HOC}_2\text{H}_4\text{OH} & \rightarrow \text{Cl-Si-O-Si-OC}_2\text{H}_4\text{OH} + \text{HCl} \\
\text{Cl} & \text{Cl} & \text{Cl} & \text{Cl} & \text{Cl} & \text{Cl}
\end{align*}
\]

Benzyl alcohol (Bibl.39) reacts energetically with silicon tetrachloride, forming benzyl chloride, silica gel, and the products of etherification. As stated above, the replacement of the OH group in benzyl alcohol by chlorine involves the liberation of water by condensation of the OH groups attached to the silicon atom. The presence of water in the reaction mixture has the result that only traces of the benzyl ester of orthosilicic acid are formed, together with a large quantity of its polymeric hydrolyzate.

Analogous phenomena were apparently observed by Dolgov and Vol'nov (Bibl.40) in their study of the reaction between nitrophenols and SiCl\textsubscript{4}. They postulate that this reaction takes place in two directions:

\[
\begin{align*}
\text{SiCl}_4 + 4\text{HOC}_2\text{H}_4\text{NO}_2 & \rightarrow \text{Si(OCH}_2\text{NO}_2)_4 + 4\text{HCl} \\
\text{SiCl}_4 + 4\text{HOC}_2\text{H}_4\text{NO}_2 & \rightarrow 4\text{ClC}_2\text{H}_4\text{NO}_2 + [\text{Si(OH)}_4]
\end{align*}
\]

They do not, however, consider that this course of the reaction has been proved. Their description of the reactions allows us to assume that polymeric products are also formed.

When SiCl\textsubscript{4} reacts with the lower organic acids or their anhydrides under cer-
tain conditions, mixed anhydrides of orthosilicic acid and organic acids may be ob-
tained.

The first report of this nature was made by Friedel and Ladenburg (Bibl.41).

\[
\begin{align*}
\text{SiCl}_4 + 4\text{CH}_3\text{COOH} & \rightarrow \text{Si(OCOCH}_3)_4 + 4\text{HCl} \\
\text{SiCl}_4 + 4(\text{CH}_3\text{CO})_2\text{O} & \rightarrow \text{Si(OCOCH}_3)_4 + 4\text{CH}_3\text{COCl}
\end{align*}
\]

Tetraacetoxysilane is a crystalline product distilling at 148°C (5-6 mm). Com-
pounds of this class react with extreme energy with water forming an organic acid
and \([\text{Si(OH)}_4]\).

When alcohol acts on tetraacetoxysilane, ethyl acetate is quantitatively
formed:

\[
\text{Si(OCOCH}_3)_4 + 4\text{C}_2\text{H}_5\text{OH} \rightarrow [\text{Si(OH)}_4] + 4\text{CH}_3\text{COOC}_2\text{H}_5
\]

The formation of \([\text{Si(OH)}_4]\) has not been established; it is most probable that
there is a reaction of substitution of the acetoxy groups by alkoxy groups according
to the formula

\[
\text{Si(OCOCH}_3)_4 + 2\text{ROH} \rightarrow \text{Si(OCOCH}_3)_4(\text{OR}) + 1\text{HCOCH}_3
\]

which has been demonstrated for the reaction of alkylacetoxysilanes with alcohols
(Bibl.41a).

K.D.Petrov has synthesized silicobutyric anhydride (Bibl.42), silicobenzoic
anhydride and silicoformic anhydride (Bibl.43).

\[
\begin{align*}
\text{SiCl}_4 + 4\text{CH}_2\text{COOH} & \rightarrow \text{Si(OCOCH}_3)_4 + 4\text{HCl} \\
\text{SiCl}_4 + 4\text{CH}_2\text{COOH} & \rightarrow \text{Si(OCOCH}_3)_4 + 4\text{HCl} \\
\text{SiCl}_4 + 4\text{HCOOH} & \rightarrow \text{Si(OCOCH}_3)_4 + 4\text{HCl}
\end{align*}
\]

He found that these products, like the anhydrides and acid chlorides, can enter into
reactions of condensation with aromatic hydrocarbons:
A better yield of ketones is obtained when the reaction is conducted in a single phase (Bibl.44) (the formation of silicoanhydrides in a medium of the corresponding aromatic solvent). By means of single-phase condensation, tolylphenyl ketone, benzophenone, methylytolyl ketone, methylychlorophenyl ketone and acetophenone in yields of 45 - 86% of theoretical have been synthesized (Bibl.44).

From the point of view of organic synthesis, the most interesting is silicofomric anhydride, since neither the anhydride nor the acid chloride of formic acid exists in the free state.

By the aid of silicofomric anhydride, the synthesis of a number of aromatic alderhydes may be accomplished, for example:

\[
\text{Si(O\text{CO}C\text{H}_3)_4 + 4\text{CH}_3\text{C}_6\text{H}_5 \xrightarrow{\text{AlCl}_3} 4\text{CH}_3\text{C}_6\text{H}_5\text{COCl} + [\text{Si(OH)}_4]}\]

The oxy group obviously reacts more easily with the atom of chlorine in \(\text{SiCl}_4\) than the carboxyl group does. Thus, oxy-acids (Bibl.45) react with SiCl₄ to form an ester, instead of a mixed anhydride:

\[
\text{SiCl}_4 + 4\text{HO(O\text{CO}OH)} \rightarrow \text{Si(O\text{ROCO})}_4 + 4\text{HCl}
\]

Ricinoleic acid, reacting by this scheme, yields silicoricinoleic acid, a viscous oily product, slowly decomposed by alkali, which can be brominated, and reacts with calcium chloride to form the calcium salt.

The presence of an active COOH group in the reaction product naturally complicates the course of the above reaction, and encourages the formation of a number of by-products (polysiloxanes, various esters, hydrides, etc.). Compounds of the type \(\text{Si(O\text{ROCO})}_4\), where \(M\) is a metal or a radical, may be obtained in better yield than \(\text{Si(O\text{ROCO})}_4\) on the reaction of \(\text{SiCl}_4\) with the salt or ester of the oxy-acid. Thus,
silicolactic acid is obtained by the reaction of SiCl₄ with zinc lactate, silico-salicylic acid by the reaction of SiCl₄ with methyl or amyl salicylate.

SiCl₄ is such an active reagent that in certain cases it can disrupt the ether bond in organic compounds.

Vol’nov (Bibl.46), studying the reactions of SiCl₄ with complex esters of acetic acid, and with various alcohols, found that the esters of the lower alcohols (up to and including amyl acetate) form silicoacetic anhydride with SiCl₄:

\[ 4CH₃COOR + SiCl₄ \rightarrow Si(OCCCH₃)₄ + 4Cl \]

Isocamyl acetate and the esters of higher alcohols, phenol and cresol, form the ester of orthosilicic acid and acetyl chloride:

\[ 4CH₃COOR + SiCl₄ \leftrightarrow Si(OR)₄ + 4CH₃COCl \]

The reaction is reversible and proceeds to completion only if the acetyl chloride is removed.

Benzyl acetate reacts differently:

\[ SiCl₄ + 2CH₃COCH₂C₆H₅ \rightarrow 2CH₃COCH₂C₆H₅ + 2C₆H₅CH₂Cl + SiO₂ \]

On the reaction of SiCl₄ with ethyl ether at boiling point, halo-esters of silicon are formed (Bibl.47).

\[ SiCl₄ + C₂H₅OC₂H₅ \rightarrow C₂H₅OSiCl₂ + C₂H₅Cl \]

This reaction makes it difficult to synthesise alkylchlorosilanes in an ether medium by Grignard’s method, since substituted esters are formed besides the alkylchlorosilanes.

When SiCl₄ reacts with esters of nitric acid (Bibl.48), a number of esters of orthosilicic acid can be obtained (Bibl.48):

\[ SiCl₄ + 4RONO \rightarrow Si(OR)₄ + 4NO₂Cl \]
The yield of product is about 80% of theoretical. If the β-chloro-ester of nitric acid is taken for the reaction, tetra-β-chloroethoxysilane is formed:

$$\text{SiCl}_4 + 4\text{CICH}_{2}\text{CHONO} \rightarrow \text{Si(OCH}_2\text{CH}_2\text{Cl})_4 + 4\text{NOCI}$$

A mixture of ethylene glycol and ethylene dinitrite (Bibl.48) reacts with SiCl₄ in the following way:

$$\begin{align*} \text{CHOH} & \quad \text{ONOCH}_2 \quad + \text{SiCl}_4 + \text{ONOCH}_2 \quad = \quad \text{CH}_2\text{O} \quad \text{OCH}_2 \quad + 2\text{HCl} + 2\text{NOCI} \\ \text{CH}_2\text{OH} & \quad \text{ONOCH}_2 \end{align*}$$

SiCl₄ reacts with esters of orthosilicic acid (Bibl.49) at temperatures of the order of 160°C:

$$\text{SiCl}_4 + 5\text{Si(OR)}_2 = 2\text{Cl}_2\text{Si(OR)}_2$$

The principal reaction product is a dialkoxydichlorosilane, but usually the trialkoxychlorosilane and the alkoxytrichlorosilane are also present. By varying the ratio between the reagents, the yield of one reaction product or the other can be increased. Tetramethoxysilane reacts with SiCl₄ at the boiling point of the mixture (Bibl.50).

Kreshkov (Bibl.51) has studied the reaction of SiCl₄ with oxy-acids obtained on the oxidation of paraffin by the oxygen of the air. He considers reaction does not take place according to the formula presented above for the oxy-acids. In his opinion, the SiCl₄ dehydrates the oxy-acids, after which it can add to the unsaturated products of dehydration at the double bond, even in the absence of a catalyst:

$$\begin{align*} \text{RCHOHCH}_2\text{CH}_2\text{COOH} + \text{SiCl}_4 & \rightarrow \text{RCH} = \text{CH} \quad \text{CH}_2\text{COOH} + [\text{Si(OH)}_4] + 4\text{HCl} \\ \text{RCH} = \text{CH} \quad \text{CH}_2\text{COOH} + \text{SiCl}_4 & \rightarrow \text{RCHCHCl} \quad \text{CH}_2\text{COOH} \quad \downarrow \text{SiCl}_4 \end{align*}$$

It must be borne in mind that even the synthesis according to Shtetter (under F-TS-9191/V 103...
pressure) involves considerable difficulties, and up to the present time has not been repeated. For this reason the hypothesis that the $\text{Si-C}$ bond is formed by simple boiling of an organic compound with silicon tetrachloride appears improbable to me. As a result of recent studies (Bibl.52) the impossibility of the addition of silicon tetrachloride at a double bond, even in the presence of a catalyst, has been proved.

The presence of a soluble product containing silicon and a small quantity of chlorine in the reaction mixture may be explained either by the formation of a poly-alkoxychlorosiloxane, or simply by the phenomena of adsorption, instead of by the formation of a compound containing the $\text{Si-C}$ bond or of addition products.

Reactions with Amines and Ketones

Silicon tetrachloride is able to react with amines, forming haloaminosilanes and aminosilanes (Bibl.53).

$$\text{SiCl}_4 + 4\text{C}_6\text{H}_5\text{NH}_2 \rightarrow \text{Cl}_2\text{Si}((\text{NH}_2\text{C}_6\text{H}_4)_2 + 2\text{C}_6\text{H}_5\text{NH}_2\text{HCl}$$

When tertiary amines react with $\text{SiCl}_4$, addition products are formed:

$$3 \text{N} + \text{SiCl}_4 \rightarrow (\text{C}_6\text{H}_5\text{N})_3\text{SiCl}_4$$

According to Dolgov and Vol'nov (Bibl.40), the reaction of paraaminophenol with $\text{SiCl}_4$ takes place in quantitative yield by the formula

$$\text{SiCl}_4 + 4\text{HCl}\text{C}_6\text{H}_4\text{NH}_2 \rightarrow \text{Si}((\text{OC}_6\text{H}_4\text{NH}_2\text{HCl})_2$$

Absolutely no compounds whatever containing the bond $\text{Si}-\text{N}$ are formed.

One peculiarity characteristic of the chemistry of silicon as a whole must be noted. The silicon atom has a large radius, thus making it capable of forming com-
plex compounds with the coordination number 6. An example of compounds of this class is the salts of fluosilicic acid. $\text{SiCl}_4$ likewise forms a number of compounds of complex structure. They include, for instance, the above mentioned compounds with tertiary amines.

$\text{SiCl}_4$ reacts well with 1,3-diketones (capable of existing in the enol form) with the formation of complex hydrochlorides:

$$3\text{CH}_3\text{COCH} = \text{C(CH}_3\text{)OH} + \text{SiCl}_4 \rightarrow \text{[CH}_3\text{COCH} = \text{C(CH}_3\text{)O}_2\text{SiCl}_3\cdot\text{HCl} + 2\text{HCl}$$

Three molecules of diketones always enter into the reaction. Dilthey (Bibl. 19), who prepared a number of such derivatives, found that one atom of chlorine in them is extremely mobile and readily enters into metathetical reactions with salts.

$$\text{[CH}_3\text{COCH} = \text{C(CH}_3\text{)OH}_2\text{SiCl}_3\cdot\text{HCl} + \text{AgNO}_3 \rightarrow \text{AgCl} + \text{[CH}_3\text{COCH} = \text{C(CH}_3\text{)O}_2\text{SiCl}_3\cdot\text{HNO}_3$$

**Alkylation Reaction of Silicon Tetrachloride**

The most important reactions of $\text{SiCl}_4$, which are responsible for its practical importance in the synthesis of organosilicon polymers, are based on its ability to replace chlorine atoms by organic radicals on reacting with certain organometallic compounds, hydrocarbons, and diazo compounds.

**Reactions with Organomagnesium Compounds**

Of the organometallic compounds that react with $\text{SiCl}_4$, the organomagnesium compounds have been most widely employed, since they are relatively more plentiful and inexpensive.

The reaction between silicon tetrachloride and organomagnesium compounds takes place according to the mechanism (Bibl. 54):

$$\text{SiCl}_4 + \text{RMgX} = \text{RSiCl}_3 + \text{MgXCl}$$
$$\text{RSiCl}_3 + \text{RMgX} = \text{R}_2\text{SiCl}_2 + \text{MgXCl}$$
The number of halogen atoms that are replaced by alkyl radicals depends on a number of conditions, the proportion between the components, the structure of the alkyl or aryl radical, the nature of the metal and the reaction conditions.

By adjusting the ratio between the quantities of SiCl₄ and organomagnesium compound, the direction may be directed toward the formation of one of the products primarily, for instance of an alkyltrichlorosilane or the dialkylidichlorosilane, but the reaction product will always also contain compounds of a greater or lesser degree of substitution. The quantity of by products depends on the relative activity of the SiCl₄ and the alkylchlorosilane with respect to the given alkylmagnesium halide; in some cases the dialkyl- or diarylidichlorosilanes are formed much more easily, in other cases the alkyltrichlorosilanes. The tetra-substituted silanes are as a rule formed with greater difficulty.

The reactions between SiCl₄ and ether solutions of the most varied organomagnesium compounds are described in the literature, for example: methylmagnesium chloride (Bibl.57), methyldimagnesium bromide (Bibl.58), methyldimagnesium iodide (Bibl.59), ethyldimagnesium chloride (Bibl.60), ethyldimagnesium bromide (Bibl.61), ethyldimagnesium iodide (Bibl.62), bromomagnesium bromide (Bibl.63), allyldimagnesium bromide (Bibl.64), butyldimagnesium bromide (Bibl.59), isooamyldimagnesium bromide (Bibl.63), hexylmagnesium bromide (Bibl.64), octylmagnesium bromide (Bibl.64), phenylmagnesium bromide (Bibl.65), cyclohexylmagnesium bromide (Bibl.66), benzylmagnesium bromide (Bibl.67), p-chlorophenylmagnesium bromide and p-bromophenylmagnesium bromide (Bibl.68), p-tolylmagnesium bromide (Bibl.69), α-naphthylmagnesium bromide (Bibl.63), and also reactions with a number of more complex organomagnesium compounds.

We have worked out a method of synthesizing organomagnesium compounds without using ethyl ether (Bibl.54). The following compounds were prepared by this method:
ethyltrichlorosilane, diethyltrichlorosilane, diisobutyltrichlorosilane, diisobutyl-
dichlorosilane, isobutyldichlorosilane, hexyltrichlorosilane, dihexyltrichlorosilane,
benzyltrichlorosilane, and α-naphthyltrichlorosilane. Vol’tnov and Reut (Bibl.56) conducted the reaction between SiCl₄ and ethylmagnesium bromide without using ethyl ether.

In runs without using ethyl ether, the yield as a rule is not lower than with the ordinary Grignard method. To prepare certain alkylchlorosilanes, working without the use of ethyl ether represents an advantage not only with respect to safety, but also in connection with the possibility of selecting a solvent allowing the reaction to be conducted at the optimum temperature.

By the successive action of different organomagnesium compounds on SiCl₄, alkyl-(aryl)-chlorosilanes and various tetra-substituted silanes may be obtained, in which unlike organic radicals are attached to the same silicon atom (Bibl.59, 64). In this case, if there are functional groups in the molecule of tetra-substituted silanes, they will be able to react both with organomagnesium compounds and with other organometallic compounds, by analogy to other organic compounds (Bibl.68):
The replacement of several chlorine atoms by branched organic radicals sometimes involves steric hindrance. For example, by the aid of isoamylmagnesium chloride, it has been possible to replace not more than two chlorine atoms (at very low yields).

On the reaction between certain organomagnesium derivatives and SiCl₄, cyclic dichlorosilane is formed:

\[ \text{BrMg(CH₃)₂MgBr} + \text{SiCl₄} \rightarrow \text{SiCl₂CH₂SiCl₂} + 2\text{MgClBr} \]

Dimagnesium derivatives of dichloroacetylene do not react with silicon tetrachloride (Bibl.70).

It has not been found possible at all to produce a reaction between SiCl₄ and tertiary organomagnesium compounds, and organolithium compounds must be used to prepare tertiary alkylchlorosilanes.

**Reactions with Organolithium Compounds**

The reaction of SiCl₄ with organolithium compounds is of great importance for the production of those organochlorosilanes of complex structure which it has not been found possible to prepare under the action of organomagnesium compounds (Bibl. 71). The reaction between silicon tetrachloride and the organolithium compound proceeds with exceptional smoothness and is very easily controlled (Bibl.72). Such compounds as tetraalkyl- or tetraarylsilanes, which can as a rule be obtained only in low yield under the action of organomagnesium compounds, are very readily obtained in high yield by using organolithium compounds instead (Bibl.73): tetraethylsilane in 92% yield, tetrabutylsilane in 98% yield, tetraphenylsilane in 99% yield.

The reaction takes place in the cold immediately after mixing the silicon tetrachloride with the solution of the organolithium compound.

Alkylchlorosilanes with branched chains can be prepared by the aid of orga-
lithium compounds; for instance, isopropyllithium yields triisopropylchlorosilane (Bibl.74) in 68% yield; while tertiary butyllithium gives tert-butyltrichlorosilane (Bibl.75) (in yield of 75%): 

\[(CH_3)_3CLi + SiCl_4 = (CH_3)_3CSiCl_3 + LiCl\]

Under the action of organolithium compounds on \(SiCl_4\), alkylchlorosilanes containing functional groups in the organic radical can be obtained, for instance (Bibl.76):

\[
\begin{align*}
&\text{Br} \quad \text{SiCl}_3 + \text{Li} \quad -
\end{align*}
\]

**Reaction with other Organometallic Compounds**

The alkylation of \(SiCl_4\) by means of organosodium compounds proceeds readily even with halo-derivatives containing no other functional groups. The reaction is very difficult to control and leads to the formation almost exclusively of tetra-substituted silanes, good yields being obtained as a rule only for the tetraarylsilanes.

Manulkin and Yakubova (Bibl.77) acting with sodium on a mixture of \(SiCl_4\) and an aryl chloride:

\[\text{SiCl}_4 + 8\text{Na} + 4\text{RCI} = \text{SiR}_4 + 8\text{NaCl}\]

obtained tetraphenylsilane (in 68% yield) and tetrabenzylsilane (in 45% yield). Tetrabiphenylsilane (Bibl.78) \(\text{Si(C}_6\text{H}_4\text{C}_6\text{H}_5)_4\) (in 60% yield) as well as tetra-p-tolyllsilane (Bibl.79) have been similarly obtained.

The aliphatic alkyl halides in the presence of sodium usually react less readily; for instance, ethyl bromide forms tetraethylsilane in insignificant yield; butylbromide hardly reacts, while isopropyl bromide and tert-butyl bromide
do not react at all (Bibl.80). There is a statement (Bibl.78) that amyl chloride forms tetraamylsilane in 80% yield. (Tetraisoamylsilane is obtained in insignificant yield) (Bibl.38).

As stated above, the reaction of alkylation by means of metallic sodium can be controlled only with great difficulty, and it has not been possible to obtain any sort of satisfactory yield of the most valuable alkylation products, the alkylchlorosilanes. It has also not been possible to conduct the reaction with halo derivatives containing other functional groups, for example with nitro- and dinitrochlorobenzene or with methoxychlorobenzene (Bibl.80), not to effect the reaction between SiCl₄ and sodium acetylide.

The possibility of performing the following reactions has been noted in the literature (Bibl.81):

$$\begin{align*}
\text{CH}_2\text{Br} & + 4\text{Na} + \text{SiCl}_4 = \text{CH}_2\text{Cl} + 4\text{NaBr} + 2\text{NaCl} \\
\text{CH}_2\text{Br} & + \text{SiCl}_4 + 2\text{Na} \\
2\text{C}_4\text{H}_9\text{Cl}_2 & + \text{SiCl}_4 + 8\text{Na} > \text{Si}\left(\text{C}_4\text{H}_9\right)_4
\end{align*}$$

subsequently, however, the formation of the latter product was not confirmed (Bibl.82).

By means of organomercury compounds, the arylchlorosilanes were first obtained (Bibl.83):

$$\text{SiCl}_4 + \text{Hg(C}_6\text{H}_5\text{)}_2 = \text{C}_6\text{H}_5\text{SiCl}_3 + \text{HgC}_6\text{H}_5\text{Cl}$$

Dimethylmercury gives practically no reaction with SiCl₄, and with dimethylzinc the reaction proceeds at a fair velocity only at temperatures over 200°C (in a sealed tube) (Bibl.84).
Diethylzinc reacts similarly.
Diethylbarium does not react with SiCl₄ (Bibl.85).

Reaction with Hydrocarbons and Diazo Compounds

Shtetter (Bibl.86) found that under a pressure of 10 - 100 atm in presence of metallic chlorides, SiCl₄ can add to compounds containing a multiple bond:

\[
\begin{align*}
\text{SiCl}_4 + \text{CH}_2=\text{CH}_2 & \rightarrow \text{Cl}_3\text{SiCH}_2\text{CH}_2\text{Cl} \\
\text{SiCl}_4 + \text{CH}:=\text{CH} & \rightarrow \text{Cl}_3\text{SiCH}=\text{CHCl} \\
\text{SiCl}_4 + \text{C}:=\text{O} & \rightarrow \text{Cl}_3\text{SiOCOCl}
\end{align*}
\]

In this case, according to data of Shtetter, workers have been able to replace only a single chlorine atom in SiCl₄. Unfortunately, during the 15 years that have passed since the publication of Shtetter's paper, no paper has appeared demonstrating convincingly enough the possibility of such a reaction, except for the patent reports, which reproduce the Shtetter synthesis without reference to the isolation of the reaction products (Bibl.87).

According to the data of Andrianov and Kochkin (Bibl.88), a mixture of SiCl₄ and a hydrocarbon can react at a temperature over 450°C:

\[
\text{RH} + \text{SiCl}_4 \rightarrow \text{RSiCl}_3 + \text{HCl}
\]

When methane reacts with SiCl₄ at 500°C, methyltrichlorosilane is formed (in 12.2% yield) and when benzene reacts with SiCl₄ at the temperature of a red heat, a certain quantity of phenyltrichlorosilane is obtained (Bibl.89).

Yakubovich and Ginzburg (Bibl.90) found that SiCl₄ can react with diazo compounds, forming mono, di, and trichloroalkylchlorosilanes.

\[
\text{SiCl}_4 + \text{CH}_2\text{N}=\cdot \rightarrow \text{Cl}_3\text{SiCH}_2\text{Cl} + \text{N}_2
\]
Reactions with Inorganic Compounds

One of the most important criteria determining the tendency of the halogen atoms attached to the silicon atom to be replaced by any other atoms is the ratio between the values of the covalent radii. As a rule substitution reactions take place readily only where the substituent atom has a smaller covalent radius than the replaced atom (Bibl.91). Accordingly, the reactions of replacement of chlorine atoms by atoms with a larger radius either do not take place at all or take place in insignificant yield. The chlorine atom \((r = 0.99 \text{ Å})\) may be replaced by the fluorine atom \((r = 0.72 \text{ Å})\), and also by the oxygen atom \((r = 0.66 \text{ Å})\) and the nitrogen atom \((r = 0.74 \text{ Å})\).

Examples of the reaction of substitution of oxygen for chlorine are all the above discussed reactions between silicon tetrachloride and water or hydroxyl-containing compounds, as well as with many inorganic compounds.

Acids hydrolyze \(\text{SiCl}_4\), for instance:

\[
\text{SiCl}_4 + 2\text{H}_2\text{SO}_4 = \text{Si(OH)}_4 + 2\text{SO}_4\text{Cl}_2
\]

Under the action of acid anhydrides or oxides of metals on \(\text{SiCl}_4\), the chlorine is replaced by oxygen, forming silica (Bibl.92) or halodisiloxane (Bibl.93):

\[
3\text{SiCl}_4 + 2\text{P}_2\text{O}_5 = 3\text{SiO}_2 + 4\text{POCl}_3
\]
\[
2\text{SiCl}_4 + \text{SO}_3 = \text{Cl}_3\text{SiOSiCl}_3 + \text{SO}_2\text{Cl}_2
\]
\[
\text{SiCl}_4 + 2\text{CaO} = \text{SiO}_2 + 2\text{CaCl}_2
\]

Examples of reactions in which chlorine is replaced by nitrogen are the reactions with amines (cf. page 104) and also the reactions between \(\text{SiCl}_4\) and isocyanates (Bibl.94) and isothiocyanates (Bibl.95).
The replacement of chlorine by fluorine takes place readily, either under the action of elementary fluorine (Bibl.92):

\[ \text{SiCl}_4 + 2F_2 = \text{SiF}_4 + 2Cl_2 \]

or under the action of antimony fluoride (Bibl.96):

\[
\begin{align*}
\text{SiCl}_4 + \text{SbF}_5 &= \text{Cl}_4\text{SiF} + \text{SbF}_6 \\
\text{Cl}_4\text{SiF} + \text{SbF}_5 &= \text{Cl}_4\text{SiF}_3 + \text{SbF}_6 \\
\text{Cl}_4\text{SiF}_3 + \text{SbF}_5 &= \text{Cl}_3\text{SiF}_3 + \text{SbF}_6 \\
\text{Cl}_3\text{SiF}_3 + \text{SbF}_5 &= \text{Cl}_3\text{SiF}_2 + \text{SbF}_6 \\
\end{align*}
\]

In this case a mixture of all the above products is formed.

In contrast to the above reactions, which take place rather actively, the substitution of chlorine by groups with a covalent radius greater than that of chlorine takes place with great difficulty. Thus, for example, the reaction of \( \text{SiCl}_4 \) with \( \text{H}_2\text{S} \) (Bibl.97) leads to the replacement of one atom of chlorine:

\[ \text{SiCl}_4 + \text{H}_2\text{S} = \text{Cl}_3\text{SiS} + \text{HCl} \]

According to recent data (Bibl.91), the yield of \( \text{Cl}_3\text{SiS} \), even at 600°C, amounts to only 1 - 2%.

Bromine and iodine do not react appreciably with silicon tetrachloride. The reaction with hydrogen bromide and hydrogen iodide takes place at a high temperature in insignificant yield:

\[ \text{SiCl}_4 + 4\text{HX} = \text{SiX}_4 + 4\text{HCl} \]

Carbon tetrabromide reacts according to the formula:

F-9191/V
\[
\text{SiCl}_4 + \text{CBr}_4 = \text{CCl}_4 + \text{SiBr}_4
\]

The yield is 12%.

The reaction of reduction of SiCl\(_4\) takes place with great difficulty. Hydrogen reacts at red heat:

\[
\text{SiCl}_4 + \text{H}_2 = \text{HSiCl}_3 + \text{HCl}
\]

Metallic sodium at 140°C does not react. The reaction:

\[
\text{SiCl}_4 + 4\text{Na} = \text{Si} + 4\text{NaCl}
\]

takes place at red heat. Metallic potassium reacts with the vapor of SiCl\(_4\) at a considerably lower temperature. The analogous reaction with silver takes place at red heat; with iron, aluminum, and magnesium, at 200 - 300°C.

Metallic magnesium does not react with SiCl\(_4\) at room temperature; heating at the boiling point for 8 hours likewise does not produce a reaction. In the presence of ethyl ether, an insignificant quantity of unstable compounds, whose structure has not been established, is formed (Bibl.98).

**Other Tetrahalosilanes**

Such silicon compounds as SiF\(_4\), SiBr\(_4\) and SiJ\(_4\) have not at the present time acquired technical importance.

The silicon atom is bound very strongly to fluorine (Bibl.99). This is evidenced by the heat of formation of SiF\(_4\) from its elements, which is 360.0 kcal/mol. It not only considerably exceeds the heat of formation of silicon tetrachloride (151.0 kcal/mol), but even the heat of oxidation of silicon (176 kcal/mol). The possibility of preparing silicon tetrafluoride from silica is connected with this. SiF\(_4\) is obtained, according to Mendeleev (Bibl.8), by treating a mixture of one part by weight of sand or glass, with one part by weight of fluorspar in 6 parts
by weight of sulfuric acid. The reaction \( \text{SiO}_2 + 4\text{HF} \rightleftharpoons \text{SiF}_4 + 2\text{H}_2\text{O} \) is reversible.

The hydrolysis of \( \text{SiF}_4 \) is an endothermic process, which, in contrast to the

\[
\text{SiF}_4 + 4\text{H}_2\text{O} \rightarrow 4\text{HF} + [\text{Si(OH)}_4] - 25.8 \text{ cal}
\]

is an endothermic process, which, in contrast to the hydrolysis of all other halo derivatives, does not proceed to completion, and some of the fluorine atoms still remain attached to the silicon.

\( \text{SiF}_4 \) is a colorless gas with a sharp odor, which fumes in the air. Its critical temperature is \(-1.5^\circ\text{C}\) and its critical pressure 50 atm. Water absorbs about 400 volumes of the gas.

Like \( \text{SiCl}_4 \), \( \text{SiF}_4 \) reacts with alcohols, forming ethers (Bibl.100):

\[
3\text{SiF}_4 + 4\text{ROH} = \text{Si}((\text{OR})_4) + 2\text{HF}
\]

This reaction, however, proceeds slowly and in low yields. The relative stability of the \(-\text{Si-F}\) bond by comparison with the stability of the \(-\text{Si-Cl}\) bond is illustrated by the fact that under the action of alcohols on fluorochlorosilanes, the fluorine remains unaffected, while the chlorine is completely replaced (Bibl.101).

\[
\text{SiCl}_4 + 2\text{C}_2\text{H}_5\text{OH} = \text{FSi}((\text{C}_2\text{H}_5)_2) + 2\text{HCl}
\]

\( \text{SiF}_4 \) reacts readily with organomagnesium compounds, however, in contrast to the reaction with \( \text{SiCl}_4 \), and in this case trialkylfluorosilanes, containing an admixture of tetramethylsilanes, are almost exclusively formed.

In 1935, Medoks and Kotelkov (Bibl.102) first studied this reaction.

\[
\text{SiF}_4 + 3\text{C}_4\text{H}_9\text{MgBr} = \text{FSi}((\text{C}_4\text{H}_9)_2) + 3\text{MgBr}
\]

When \( \text{SiF}_4 \) reacts with phenylmagnesium bromide, tetraphenylsilane is not formed;
benzylmagnesium chloride, according to the data of Medoks (Bibl.103), reacts with SiF₄, forming a mixture of tribenzylfluorosilane and tetrabenzylsilane.

The reaction of SiF₄ with ethylmagnesium bromide, propyl-, butyl-, and amylmagnesium chloride (Bibl.104) takes place with the formation of a mixture of tri- and tetra-substituted products.

Silicon tetrabromide is obtained by the reaction between bromine and silicon (Bibl.105), and on the action of bromine on a mixture of silica with coal or magnesium at a high temperature. SiBr₄ is a liquid of specific gravity 2.82, boiling point 151.8°C, melting point 12 - 15°C, refractive index nD²³.₅ = 1.56267.

The strength of the -Si-Br- bond is considerably less than that of the -Si-F bond, and therefore SiBr₄ usually reacts more actively. Thus, for instance, the reaction of SiBr₄ with metallic potassium at ordinary temperatures is explosive.

Yakubovich and Ginsburg (Bibl.90) described the reaction of SiBr₄ with diazo compounds. This reaction takes place readily at temperatures of an order of -70°C, forming di- and tri-a-bromoalkylbromosilanes:

\[
\text{SiBr}_4 + 2\text{CH}_2\text{N}_2 \rightarrow (\text{BrCl}_2)_2\text{SiBr}_2 + 2\text{N}_2
\]

On the action of antimony trichloride on SiBr₄, the bromine is replaced by chlorine (Bibl.110), and both chlorobromosilanes and SiCl₄ may be obtained. In contrast to the reaction with SiCl₄, the reaction of hydrogen sulfide with SiBr₄ takes place readily and in good yield (Bibl.91).

\[
\text{SiBr}_4 + \text{H}_2\text{S} = \text{Br}_2\text{SiSH} + \text{HBr}
\]

The iodine atom is bound still less strongly to silicon:

\[
\text{Si} + 2\text{I}_2 = \text{SiI}_4 (+ 6.7 \text{cal})
\]

This reaction (Bibl.106) usually takes place under the action of iodine on
silicon in a stream of carbon dioxide at a temperature of the order of 500°C, or under the action of iodine on a mixture of silica and magnesium.

Tetraiodosilane is a crystalline substance readily soluble in carbon disulfide; melting point 120.5°C; boiling point 290°C. The product is readily distilled in a stream of carbon dioxide gas. In the air SiI₄ vapor spontaneously ignites:

\[ \text{SiI}_4 + 2\text{O}_2 = \text{SiO}_2 + 2\text{I}_2 \]

When SiI₄ reacts with alcohols, esters are not formed.

\[ \text{SiI}_4 + 2\text{C}_2\text{H}_5\text{OH} = \text{SiO}_2 + 2\text{C}_2\text{H}_5\text{I} + 2\text{H}_2\text{O} \]

Ethyl ether reacts with tetraiodosilane according to the formula:

\[ \text{SiI}_4 + 4(\text{C}_2\text{H}_5)\text{O} = 4\text{C}_2\text{H}_5\text{I} + \text{Si}((\text{OC}_2\text{H}_5)_4 \]

There is an indication that when iodosilanes react with magnesium in the presence of ethyl ether, unstable silylmagnesium iodides are formed (Bibl.107).

As a result of the fact that the covalent radii of the bromine atom (1.14 Å) and of the iodine atom (1.33 Å) are greater than the radii of the atoms of fluorine, nitrogen, oxygen, and sulfur, it follows that bromine and iodine are readily replaced by these atoms. Thus, under the action of the antimony trifluoride on SiBr₄, one, two, three or four atoms of bromine may be replaced by fluorine. SiI₄ reacts similarly. Bromine, like chlorine, may be easily replaced by an isocyanato group (Bibl.109).

\[ \text{SiCl}_2\text{Br}_2 + 4\text{AgNCO} = \text{Si(NCO)}_4 + 2\text{AgBr} + 2\text{AgCl} \]

The mixed tetrahalosilanes (Bibl.111) may be prepared by the following methods:

1. By the action of a hydrogen halide on a tetrahalosilane at high temperatures:

\[ \text{SiCl}_4 + \text{HBr} = \text{SiCl}_3\text{Br} + \text{HCl} \]

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2. By the action of an elementary halogen on mono-, di-, and trihalosilanes:

\[ \text{HSiCl}_3 + \text{Br}_2 = \text{BrSiCl}_3 + \text{HBr} \]

3. By the action of hydrogen chloride or bromide on silicon.

4. By heating a mixture of two tetrahalosilanes in a sealed tube. Thus, for instance, as a result of heating a mixture of equal volumes of SiCl\(_4\) and SiBr\(_4\) for 70 hours at 140°C, a mixture of chlorobromosilanes is formed.

5. By the action of antimony trichloride or trifluoride on tetrahalosilanes (SiBr\(_4\) or SiI\(_4\)).

Table 4 gives the molecular volumes, the energies of ionization, the bond refractions and the bond lengths of the tetrahalosilanes.

### Table 4

<table>
<thead>
<tr>
<th></th>
<th>a)</th>
<th>b)</th>
<th>c)</th>
<th>d)</th>
<th>e)</th>
<th>f)</th>
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<tr>
<td>Silicon Tetrafluoride</td>
<td>SiF(_4)</td>
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<td>102</td>
<td>1.80</td>
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<td>Silicon Tetraisodide</td>
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<td>121.7</td>
<td>92</td>
<td>15.53</td>
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</table>

a) Name; b) Formula; c) Molecular Volume, cc; d) Energy of Ionization (Formation of Singly-Charged Ion), kcal; e) Bond Refraction, cm\(^3\); f) Bond Length, Å

The physical properties of the tetrahalogenated silanes are given in Table 5.
Table 5

Physical Properties of the Tetrahalosilanes

<table>
<thead>
<tr>
<th></th>
<th>a)</th>
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<tr>
<td>Tetrafluorosilane</td>
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<td>Tetramethylsilane</td>
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<td>156</td>
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<td>156</td>
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<td>Difluorodibromosilane</td>
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<td>Dihalodihalosilane</td>
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<td>111,144</td>
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<tr>
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<td>111</td>
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<td>230-231</td>
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<td>Tribromodihalosilane</td>
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<td>54</td>
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</table>

a) Name; b) Formula; c) Melting Point, °C; d) Boiling Point °C;

e) Specific Gravity; f) Bibliography

MONO-, DI-, AND TRIHALOSILANES

Mono-, di-, and trihalosilanes possess the properties of both the halo-derivatives of silicon and of the silanes. The replacement of a hydrogen atom in the silanes by a halogen atom stabilizes the molecule of the compound; in contrast to the silanes, the halosilanes as a rule are unable to ignite spontaneously in air. The stability of the halosilanes increases with the number of halogen atoms.

The trihalosilanes HSiX₃ are relatively stable substances, and thus their synthesis can be accomplished with considerably greater ease than the synthesis of mono- and dihalosilanes. The practical importance of the trihalosilanes, and above all that of trichlorosilane, is due primarily to the formation of these products as impurities in the direct synthesis of alkylchlorosilanes, and to their ability to replace hydrogen by an organic radical in reactions with unsaturated hydrocarbons.
Methods of Preparation

The most convenient method of preparing halosilanes (mainly the trihalosilanes) is based on the reaction between a hydrogen halide and silicon or ferrosilicon at a high temperature (Bibl.112). The use of metals, including copper, does not improve the yields of the products, and does not help to lower the temperature of synthesis.

Preparation of trichlorosilane ("silicochloroform") $\text{HSiCl}_3$ (Bibl.113). 375 g of 90% silicon is ground to lumps about 1 cm in size, and is charged into a tube of refractory glass or quartz, 30 mm in diameter and 450 mm long. The tube is heated to a temperature of about 300°C; at this temperature a stream of dried nitrogen is passed for 24 hours; the temperature is then raised to 350°C and a stream of dry hydrochloric acid is passed through the tube. The rate of flow of the HCl is 0.6 - 0.85 mol per hour. After the condensate begins to form, the temperature is gradually reduced to 290 - 310°C. At intervals of 10 hours, the stream of HCl is turned off and a current of dry nitrogen is blown through the tube for 10 minutes. The reaction product is collected in a receiver cooled with solid carbon dioxide; 1370 g of condensate can be obtained in the course of 60 hours. On rectification of the condensate in a column with 15 theoretical plates, 1045 g of trichlorosilane is obtained; boiling point 31.5 - 32°C (at 729 mm). $\text{SiCl}_4$ and a small quantity of dichlorosilane $\text{H}_2\text{SiCl}_2$ and hexachlorodisilane $\text{Si}_2\text{Cl}_6$ are formed as by-products. An increase in the rate of flow of HCl, or an increase of the temperature in the tube to 360 - 370°C, leads to a considerable drop in the yield of trichlorosilane, and increases the $\text{SiCl}_4$ content of the condensate.

The reaction between silicon and HBr is conducted by a similar method (Bibl.114), but at a higher temperature (360°C). The reaction product contains 2.8% of dibromosilane $\text{H}_2\text{SiBr}_2$, 66.1% of tribromosilane $\text{HSiBr}_3$, and 31% of $\text{SiBr}_4$. The increase of the temperature in this reaction has less effect on the yield than in the preparation of trichlorosilane; the condensate obtained at 470°C contains 45% of tribromosilane and 55% of $\text{SiBr}_4$. A change in the rate of flow of the HBr likewise
fails to exert any substantial influence on the yield.

Another method of preparing halosilanes is the hydrogenation of tetrahalosilanes in the vapor phase (Bibl.115). This process is performed by passing the vapor of the tetrahalosilane mixed with hydrogen over a ground metal capable of accepting the halogen, for example over aluminum or zinc. The reaction temperature reaches about 400°C. From SiCl₄, under these conditions, 20% of trichlorosilane and 3 - 5% of dichlorosilane is obtained:

\[
2\text{SiCl}_4 + \text{H}_2 + \text{Zn} \rightarrow 2\text{HSiCl}_3 + \text{ZnCl}_2 \\
2\text{HSiCl}_3 + \text{H}_2 + \text{Zn} \rightarrow 2\text{H}_2\text{SiCl}_3 + \text{ZnCl}_2
\]

Trifluorosilane is obtained by the incomplete fluorination of trichlorosilane (Bibl.118) by tin tetrafluoride, titanium tetrafluoride (at 100-120°C), or by antimony trifluoride in the presence of antimony pentachloride. The latter reaction takes the most quiet course.

The considerably less stable mono- and difluorosilanes, as well as the intermediate products of fluorination, fluorochlorosilanes, may be prepared from mono- and dichlorosilanes by a similar reaction. The fluorination of trichlorosilane without the use of SbCl₅ leads to the formation of SiF₄ (Bibl.116):

\[
3\text{HSiCl}_3 + 4\text{SbF}_5 \rightarrow 3\text{SiF}_4 + 2\text{Sb} + 25\text{SbCl}_3 + 3\text{HCl}
\]

The preparation of mono- and dihalosilanes is in general more complicated, owing to their instability. The only process with a quiet course, with more or less good yields, is the halogenation of silane by a gaseous hydrogen halide in the presence of aluminum chloride (Bibl.117, 118). In this case a mixture of products of various degrees of substitution is formed:

\[
\text{SiH}_4 + \text{HX} \rightarrow \text{SiH}_4\text{X} + \text{H}_2 \\
\text{H}_3\text{SiX} + \text{HX} \rightarrow \text{H}_3\text{SiX}_2 + \text{H}_2
\]
Reactions of this type are characteristic only for silicon and are evidently possible as a result of the weakness of the \(-\text{Si-H}\) bond. The reaction temperature of HCl and HBr with silanes reaches 100°C, that of HI (in the presence of aluminum iodide) runs up to 80°C.

**Physical Properties**

Table 6 gives the physical properties of mono, bi and trihalosilanes.

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c)</th>
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<th>e)</th>
<th>f)</th>
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<tr>
<td>Difluorosilane</td>
<td>SiHF₂</td>
<td>-119.1</td>
<td>-77.5</td>
<td>-</td>
<td>118</td>
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<td>SiH₂F₃</td>
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<td>-97.0</td>
<td>-</td>
<td>149</td>
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<td>Tribromosilane</td>
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<td>-73.5</td>
<td>111.8</td>
<td>2.312</td>
<td>147</td>
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<td>Iodosilane</td>
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<td>-18.4</td>
<td>-</td>
<td>145</td>
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</table>

a) Name; b) Formula; c) Melting Point, °C; d) Boiling Point, °C;

e) Specific Gravity; f) Bibliography

The physical properties of the halosilanes depend on the nature of the halogens and on their number in the molecule; thus, monochloro and dichlorosilanes, as well as monofluoro and difluorosilanes, are gases under ordinary conditions; trichloro-
Silanes, monobromosilane and moniodosilane are highly volatile liquids; and dibromo and tribromosilanes are also liquids, but with a higher boiling point.

Chemical Properties

As already stated, the halosilanes are exceptionally reactive compounds, which combine the properties of the silanes and the tetrahalosilanes. Like the tetrahalosilanes, they are energetically hydrolyzed by water, forming polysiloxanes. The compounds obtained on hydrolysis contains Si-H bonds, whose number is usually somewhat smaller than in the starting monomer. The mono and dihalosilanes form disiloxane in the first phase of hydrolysis:

\[
\begin{align*}
2H_xSiX + H_2O &\rightarrow 2HX + H_xSiOSiH_x \\
2H_xSiX_2 + 3H_2O &\rightarrow 4HX + (HO)H_xSiOSiH_x(OH)
\end{align*}
\]

This compound is then decomposed, giving off hydrogen and forming a polysiloxane containing less than two atoms of hydrogen attached to the silicon. The trihalosilanes are hydrolyzed to form polysiloxanes containing hydrogen attached to the silicon atom:

\[
xH_xSiX_3 + 1.5xH_2O \rightarrow (HO)SiO_xH_x(OH) \rightarrow 3HCl
\]

D.I.Mendeleyev obtained a leuconed by the hydrolysis of silicochloroform, and regarded it as an oxysilane (Bibl.8).

The hydrolysis of fluorosilane proceeds somewhat differently. When fluorosilanes react with water, HF is formed at the first instant, and, as is well known, easily disrupts the bonds between the silicon atoms and the atoms of most elements. As a result of the hydrolysis, a number of substances are obtained: hydrogen, fluosilicic acid, and a polysiloxane containing a very small number of Si-H bonds.

In the molecule of mono, di, or trihalosilane, the halogen attached to the silicon atom has the same properties as the halogen atom in the tetrahalosilane.
molecule - the halogen is not only subject to hydrolysis, but is also easily replaced by alkoxy groups, and reacts with organomagnesium compounds, etc. In these cases, the -Si-H bonds, as a rule, are preserved (in the absence of alkalies, HF or oxidants).

When a benzene solution of trichlorosilane reacts with alcohols, trialkoxysilanes may be obtained:

$$\text{HSiCl}_3 + 3\text{ROH} = \text{HSi(OR)}_3 + 3\text{HCl}$$

In this way triethoxy, tripropoxy, and tributoxysilanes (Bibl.38), as well as various esters of higher alcohols have been prepared (Bibl.119). Tetraalkoxysilanes are always formed as a byproduct of the reaction, and in the absence of a solvent the yield of trialkoxysilanes is considerably lower, and the main product of the reaction is a tetraalkoxysilane.

On the reaction of trichlorosilane with methylmagnesium bromide (Bibl.120), with ethyl-, phenyl-, or benzylmagnesium bromide (Bibl.121), and also with organomagnesium compounds with a longer carbon chain, (up to C₁₈) (Bibl.122), products of the partial or total alkylation of trichlorosilane are formed, preserving the -Si-H bonds.

$$\text{HSiCl}_3 + \text{RMgX} \rightarrow \text{HSiR}_3 + \text{MgCl}_2$$

Under the action of metallic sodium on a mixture of trichlorosilane and alkyl halides, trialkylsilanes are formed, for instance triisobutylsilane and triisooctylsilane (Bibl.38).

The reaction of halosilanes with dialkylzinc likewise leads to the formation of...
alkylsilanes (Bibl.117).

\[ \text{H}_2\text{SiCl}_3 + \text{Zn}(\text{CH}_3)_2 = \text{H}_2\text{SiCl}_3 + \text{Zn}(\text{H}_2)_3 \]

The mono-, di-, and trihalosilanes, like the silanes themselves, oxidize readily.

\[ -\text{Si}-\text{H} + \text{O} \rightarrow -\text{Si}-\text{OH} \]

They are therefore strong reducing agents, like the silanes.

When mono-, di-, or trichlorosilanes react with strong alkalis (best of all with 30% KOH), the hydrolysis is accompanied by the quantitative destruction of the \(-\text{Si-H}\) bonds, a hydrogen molecule being liberated at each of them:

\[ -\text{Si}-\text{H} + \text{KOH} \rightarrow -\text{Si}-\text{OK} + \text{H}_2 \]

The determination of the number of \(-\text{Si-H}\) bonds in silicon compounds is based on this reaction.

The halosilanes have a tendency, which they share with most silicon compounds, to form symmetrical molecules when heated:

\[ 4\text{HSiCl}_3 \rightarrow 3\text{SiCl}_4 + \text{SiH}_4 \]

It has recently been found (Bibl.123) that unsaturated compounds may add to halosilanes (as well as to alkylhalosilanes) at temperatures lower than the decomposition points of the unsaturated hydrocarbon.

\[ -\text{Si}-\text{H} + \text{RCH}=\text{CHR'} \rightarrow -\text{Si}--\text{CHRCH}_2\text{R'} \]

This process readily takes place in the presence of peroxides, or when the
compounds are irradiated with ultraviolet light. Under these conditions, the weak 
-Si-H bond is broken, thus creating the conditions for the formation of the -Si-C bond. Trichlorosilane reacts most easily of all with n-octene; and octyltrichlorosi-
lane is formed by this reaction:

\[
\text{CH}_3\text{SiH} + \text{CH}_2=\text{CHC}_9\text{H}_3 \rightarrow \text{CH}_3\text{SiC}_9\text{H}_{17}
\]

Methyldichlorosilane \(\text{CH}_3\text{SiHCl}_2\), dimethylchlorosilane \((\text{CH}_3)_2\text{SiHCl}\) and many other alkylchlorosilanes, react similarly, and a number of alkylchlorosilanes with complex carbon radicals can be obtained in this way.

When the reaction is run at a temperature of the order of 500°C, pyrolysis of the unsaturated compound may take place; when trichloroethylene, for example, reacts with trichlorosilane, dichlorovinyltrichlorosilane is formed (Bibl.124):

\[
\text{Cl}_2\text{C} = \text{Cl} + \text{HCl} \rightarrow \text{ClC} = \text{CCl} + \text{HCl} \\
\text{ClC} = \text{CCl} + \text{HSiCl}_3 \rightarrow \text{ClC} = \text{CClSiCl}_3
\]

Alkylenechlorosilanes may also react with chlorosilanes, for instance (Bibl.125):

\[
\text{HSiCl}_3 + \text{CH}_2\text{Si} = \text{CH} = \text{CH}_2 \rightarrow \text{Cl}_2\text{SiCH}_2\text{CH}_2\text{SiCl}_3
\]

forming compounds containing organic radicals between the silicon atoms.

Trichlorosilane may add to the double bonds of rubber. This reaction is con-
ducted in a benzene solvent at temperatures of the order of 300°C and pressures of about 60 atm (Bibl.126).

When trichlorosilane reacts with benzene at temperatures of 750 - 770°C, a small quantity of phenyltrichlorosilane (Bibl.127) may be formed. The reaction be-
tween trichlorosilane and ethyl chloride takes place at 320°C and 130 atm:

\[
\text{HSiCl}_3 + \text{C}_2\text{H}_5\text{Cl} \rightarrow \text{C}_2\text{H}_5\text{SiCl}_3 + \text{HCl}
\]
OXIDATION OF HALOSILANES INTO POLYHALOSILOXANES

The oxidation of the halo-derivatives of silicon at elevated temperatures by the oxygen of the air leads to the formation of a mixture of polyhalosiloxanes. The end product of oxidation is SiO_2.

The greater affinity of the silicon atom for oxygen than for iodine, chlorine, or bromine, is expressed in the difference between the heat of formation of the respective compounds from the elements:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Heat of Formation, kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO_2</td>
<td>205</td>
</tr>
<tr>
<td>SiF_4</td>
<td>360</td>
</tr>
<tr>
<td>SiCl_4</td>
<td>151</td>
</tr>
<tr>
<td>SiBr_4</td>
<td>71</td>
</tr>
<tr>
<td>SiI_4</td>
<td>7</td>
</tr>
</tbody>
</table>

It will be seen from these data that the oxidation of chlorides, bromides and iodides of silicon must be accompanied by the liberation of heat, while the oxidation of silicon fluoride must take place with a considerable absorption of heat. Direct measurements of the heat of oxidation of halo-substituted silanes have not been made.

The reaction of tetrahalosilane with oxygen in the initial stage of the reaction can be expressed by the equations:

\[
4\text{SiX}_4 + \text{O}_2 = 2\text{X}_2\text{SIOX}_3 + 2\text{X}_2
\]

\[
2\text{X}_2\text{SIOX}_3 + 2\text{SiX}_4 + \text{O}_2 = 2\text{X}_2\text{SIOX}_2\text{OSiX}_3 + 2\text{X}_2
\]

Linear and cyclical polyhalosiloxanes are subsequently formed. On the oxidation of SiCl_4 (Bibl.129), the optimum temperature for obtaining the intermediate
reaction products is 950-970°C. Of the reaction products obtained on the inter-
action of SiCl₄ vapor with oxygen, hexachlorodisiloxane and octachlorocyclotetrasi-
loxane have been isolated. At a still higher temperature, silica is obtained:

\[ \text{SiCl}_4 + O_2 \rightarrow \text{SiO}_2 + 2\text{Cl}_2 \]

For the oxidation of SiBr₄ into polybromosiloxanes, the optimum reaction tem-
perature must be 670-695°C. When a mixture of SiCl₄ vapor with oxygen is passed
through a tube heated to that temperature, a mixture of SiBr₄ and oxidation products
(Bibl.130) of the following composition is obtained:

<table>
<thead>
<tr>
<th>Product</th>
<th>Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexabromodisiloxane [Br₃SiOSiBr₃]</td>
<td>14.4</td>
</tr>
<tr>
<td>Octabromotrisiloxane [Br₃SiOSiBr₂OSiBr₃]</td>
<td>29.6</td>
</tr>
<tr>
<td>Octabromocyclotetrasiloxane [(SiOBr₂)₄]</td>
<td>30.4</td>
</tr>
<tr>
<td>Decabromotetrasiloxane [Br₃SiO(SiOBr₂)₂SiBr₃]</td>
<td>10.4</td>
</tr>
<tr>
<td>Dodecabromopentasiloxane [Br₃SiO(SiOBr₂)₃SiBr₃]</td>
<td>9.6</td>
</tr>
</tbody>
</table>

The oxidation of SiBr₄ by ozone, or by heated silver oxide, leads only to the
formation of silica.

The oxidation of the halosilanes has been very little studied. By means of the
photochemical oxidation of trichlorosilane, trichlorohydroxysilane has been obtained
(Bibl.10):

\[ \text{HSiCl}_3 + \text{O} \rightarrow \text{HOSiCl}_3 \]

The product is easily condensed into hexachlorodisiloxane and is readily
hydrolyzed.

On the oxidation of tribromosilane HSiBr₃, silica is formed at temperatures as
low as 90°C, together with HBr and the hydrolyzate of tribromosilane, polyhydrosil-
oxane (Bibl.130) (HSiOl₅)ₓ. It has not been possible to isolate the intermediate
oxidation products.

The halosilanes containing more than one hydrogen atom attached to the silicon atom are very energetically oxidized and usually ignite spontaneously in the air.

Preparation of Halosiloxanes from Silicon and a Mixture of Halogen and Oxygen

The most convenient method of preparing the halosiloxanes is the action of a mixture of halogen and oxygen on silicon. When chlorine and oxygen (in volume ratio 2:1) is passed over porcelain at a temperature of the order of 800°C, a mixture containing a number of silicon oxychlorides is formed, from which hexachlorodisiloxane, octachlorotrisiloxane, octachlorocyclotetrasiloxane, decachlorotetrasiloxane, dodecachloropentasiloxane, tetradechlorehexasiloxane, and hexadecachloropentasiloxane have been isolated by rectification (Bibl.131). The analogous reaction with bromine at 700°C forms a mixture (Bibl.130) containing SiBr₄ and the following polybromosiloxanes:

<table>
<thead>
<tr>
<th>Yield, %</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hexabromodisiloxane Si₂OBr₆</td>
<td>20.6</td>
<td>Octabromotrisiloxane Si₃O₂Br₄</td>
<td>49.4</td>
<td>Octabromocyclotetrasiloxane Si₄O₄Br₈</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Decabromotetrasiloxane Si₄O₄Br₁₀</td>
<td>12.4</td>
<td>Dodecabromopentasiloxane Si₅O₄Br₁₂</td>
<td>10.3</td>
<td>Higher Polybromosiloxanes</td>
<td>6.2</td>
<td></td>
</tr>
</tbody>
</table>

The Properties of Halosiloxanes

The polyhalosiloxanes, being acid chlorides of the polysilicic acids, are completely analogous to the tetrahalosilanes in their chemical properties. The reactions of the hydrolysis of these compounds proceed according to the same pattern as the hydrolysis of tetrahalosilanes, which has been considered in detail on the example of SiCl₄, the rate of hydrolysis being considerably decreased with increasing length of the siloxane chain (Bibl.131). The reaction with hydroxyl-containing
compounds proceeds in the same way as with the tetrahalosilanes, but at a slower rate. Thus, the reaction of hexachlorodisiloxane with alcohols:

\[
\text{Cl}_4\text{SiOSiCl}_3 + 6\text{C}_2\text{H}_5\text{OH} = (\text{C}_4\text{H}_9\text{OSi}((\text{C}_2\text{H}_5)_2\text{Si})_3 + 6\text{HCl}
\]

if the HCl is removed (by aspirating dry nitrogen through the reaction mixture), is completed only at 105°C. The analogous reaction with octachlorotrisiloxane is completed at 125°C, and with tetradecachlorohexasiloxane (Bibl.132), at 160°C.

When hexachlorodisiloxane reacts with alcohol, considerable amounts of tetraalkoxysilanes may be obtained, besides the polyalkoxysiloxanes (Bibl.133).

\[
2\text{SiCl}_4 + 12\text{ROH} \rightarrow \text{Si(OR)}_3 + (\text{RO})_2\text{SiOSi(OR)}_2 + 12\text{HCl}
\]

The formation of tetraalkoxysiloxanes may be explained by the fact that the HCl liberated during the reaction helps to disrupt the siloxane bond.

The esterification of polylbromosiloxanes by alcohol is very difficult to accomplish, since the HBr liberated reacts readily with the alcohol, thus forming water, which hydrolyzes the -Si-Br bond. This reaction may be effected (Bibl.130) by the action of sodium alcoholate on polybromosiloxane.

The action of halosiloxanes on organometallic compounds leads to the formation of organohalosiloxanes or organosiloxanes. Thus, when hexachlorodisiloxane reacts with ethylmagnesium bromide, from 1 to 6 chlorine atoms can be replaced (Bibl.134):

\[
\text{Cl}_4\text{SiOSiCl}_3 + \text{C}_2\text{H}_5\text{MgBr} \rightarrow \text{C}_4\text{H}_9\text{SiCl}_2\text{OSiCl}_3 + \text{MgClBr}
\]

The reaction of hexachlorodisiloxane with methylmagnesium iodide and phenylmagnesium bromide takes a similar course.

When hexachlorodisiloxane reacts with haloalkyl and metallic sodium (Bibl.78), the siloxane bond is split, forming tetraalkyl-(tetraaryl)-silanes. If this process is conducted in two stages, however, the derivative of disiloxane is the principal
product (Bibl.135):

\[
\begin{align*}
\text{C}_4\text{H}_4\text{Cl} + 2\text{Na} &= \text{C}_4\text{H}_4\text{Na} + \text{NaCl} \\
\text{Cl}_4\text{SiOSiCl}_4 + 6\text{C}_4\text{H}_4\text{Na} &= \text{(C}_4\text{H}_4)_2\text{SiOSi(C}_4\text{H}_4)_2 + 6\text{NaCl}
\end{align*}
\]

Diethylzinc reacts with hexachlorodisiloxane to form a mixture of hexaethyldisiloxane and tetraethylsilane (Bibl.136).

The halosiloxanes are thermally stable compounds; thus, when hexabromodisiloxane is heated (Bibl.130), it begins to decompose only at a temperature above 260°C:

\[2\text{SiOB}_3 = 3\text{Br}_2 + \text{SiO}_2\]

Table 7 gives the physical properties of the polyhalosiloxanes.

**Table 7**

**Physical Properties of Low Molecular Polyhalosiloxanes**

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c)</th>
<th>d)</th>
<th>e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decachlorodisiloxane</td>
<td>Si_2Cl_10</td>
<td>109-110.0 (15 mm)</td>
<td>131</td>
<td></td>
</tr>
<tr>
<td>Dodecafluoropentasiloxane</td>
<td>Si_2F_12</td>
<td>130-131 (15 mm)</td>
<td>131</td>
<td></td>
</tr>
<tr>
<td>Tetradechlorohexamasiloxane</td>
<td>Si_4Cl_14</td>
<td>130-141 (15 mm)</td>
<td>131</td>
<td></td>
</tr>
<tr>
<td>Hexafluoropentasiloxane</td>
<td>Si_3F_10</td>
<td>145-147 (15 mm)</td>
<td>131</td>
<td></td>
</tr>
<tr>
<td>Pentafluorochlorodisiloxane</td>
<td>Si_2FCl_3</td>
<td>118 (15 mm)</td>
<td>130</td>
<td></td>
</tr>
<tr>
<td>Trifluorochloro-</td>
<td>SiCl_3</td>
<td>17.5 ± 0.2</td>
<td>150 (12 mm)</td>
<td>130</td>
</tr>
<tr>
<td>Tetrafluorochlorodisiloxane</td>
<td>Si_4Cl_14</td>
<td>125-135 (7 mm)</td>
<td>130</td>
<td></td>
</tr>
<tr>
<td>Hexachloropentasiloxane</td>
<td>Si_3Cl_10</td>
<td>118 (15 mm)</td>
<td>130</td>
<td></td>
</tr>
<tr>
<td>Dodecafluoropentasiloxane</td>
<td>Si_2F_12</td>
<td>130-131 (15 mm)</td>
<td>131</td>
<td></td>
</tr>
<tr>
<td>Tetrabromotetrasiloxane</td>
<td>SiBr_24</td>
<td>165-170 (0.5 mm)</td>
<td>130</td>
<td></td>
</tr>
<tr>
<td>Pentafluorodisiloxane</td>
<td>Si_2FCl_3</td>
<td>122 (0.5 mm)</td>
<td>130</td>
<td></td>
</tr>
<tr>
<td>Trifluorocyclosiloxane</td>
<td>SiF_3</td>
<td>82 ± 2</td>
<td>150 (0.5 mm)</td>
<td>130</td>
</tr>
<tr>
<td>Tetrafluorodisiloxane</td>
<td>Si_4F_14</td>
<td>78</td>
<td>160-180 (0.5 mm)</td>
<td>130</td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Melting Point °C; d) Boiling Point °C; e) Bibliography
HALOSUBSTITUTED POLYSILANES

As has already been pointed out, the direct bond between two silicon atoms is very unstable; the strength of such bonds depends primarily on the atoms or groups with which the remaining valences of the silicon are bound. The derivatives of the polysilanes are fairly stable only where all the valences of the silicon not bound to neighboring silicon atoms are bound to atoms of halogen or organic radicals, especially with phenyl radicals. The instability of polyhalosilanes increases with the number of silicon atoms in the chain, and the preparation of substituted higher silanes therefore involves certain difficulties.

The simplest method of preparing polychlorosilanes is the chlorination of silicon or ferrosilicon at 180 - 200°C. According to the data of Martin (Bibl.2), the reaction products contain, in addition of SiCl₄, 5.1% of Si₂Cl₆ and 0.35% of Si₃Cl₈, as well as a slight quantity of higher polychlorosilanes.

Another method of preparing polyhalosilanes is the condensation of trihalosilanes HSiX₃ under the action of an electric glow discharge (Bibl.137). Trichlorosilane yields a mixture of polychlorosilanes up to Si₆Cl₁₄; tribromosilane, a mixture of polybromosilanes up to and including Si₄Br₁₀.

Hexabromodisilane is formed in high yield by the action of bromine or a mixture of bromine and oxygen on calcium silicide (Bibl.137).

Hexaiodosilane (Bibl.138) was obtained earlier than other hexahalosilanes by heating tetraiodosilanes with silver dust at 300°C:

\[ 2SiI₄ + 2Ag \rightarrow I₄SiI₄ + 2AgI \]

When mercuric chloride acts on hexaiodosilane, hexachlorodisilane may be obtained:

\[ Si₄I₄ + 3HgCl₂ \rightarrow Si₄Cl₄ + 3HgI₂ \]
and when bromine acts on it, hexabromodisilane:

\[ \text{Si}_6\text{J}_6 + 3\text{Br}_2 \rightarrow \text{Si}_6\text{Br}_6 + 3\text{J}_2 \]

The most convenient method of preparing hexafluorodisilane (together with tetrafluorosilane) is the fluorination of hexachlorodisilane by anhydrous zinc fluoride.

There are statements that under the action of tetrahalosilanes on silicon at a high temperature, polyhalosilanes are formed (Bibl.139). In this way hexachlorodisilane and hexafluorodisilane have been obtained. Relatively recently (Bibl.140) polysilanes containing ten directly connected silicon atoms in the molecule have been described. These products were prepared by passing \( \text{SiCl}_4 \) in a stream of inert gas or hydrogen through a furnace filled with silicon rods. The reaction takes place at 1000 - 1100°C. The reaction product is a viscous liquid distilling in a high vacuum at 215 - 220°C. The method of analysis of this product, its elementary composition, molecular weight (cryoscopic), and number of bonds and number of \(-\text{Si-H}\) and \(-\text{Si-Si-}\) bonds (by treatment with alkali) are described in detail. On the basis of the analytical data, the authors of this paper assign the formula \( \text{Si}_{10}\text{Cl}_{22} \) to the product of the reaction of \( \text{SiCl}_4 \) with silicon in a stream of inert gas, and the formula \( \text{Si}_{10}\text{Cl}_{20}\text{H}_2 \) to the product obtained in a stream of hydrogen.

On pyrolysis of these products, an insoluble hard polymer containing equimolecular quantities of chlorine and silicon, and stable against the action of oxygen up to a temperature of 98°C, is formed. It is not possible to elucidate the structure of the polymer on the basis of the data given in this paper alone. It is difficult to agree with the formula given \(-\text{Si-Si-Si-Si-}\); the formation of high-molecular space polymers should, in preference, be supposed.

Most polyhalosilanes are solid crystalline substances; only the polychlorosil-
anes, up to and including \( \text{Si}_5\text{Cl}_{12} \) are liquids, while hexafluorodisilane is a gas.

Like the halosilanes, the polyhalosilanes readily hydrolyze to form polysiloxanes. The chlorine atom enters into all reactions characteristic of the halosilanes and described above (cf. page 92). In addition, a number of the chemical properties of polyhalosilanes are due to the presence of the \(-\text{Si}-\text{Si}-\) bond, for example, all these compounds are easily oxidized when heated in air.

The oxidation of polyhalosilanes lead to the formation of silica (Bibl.130).

\[
2\text{Si}_2\text{Br}_6 + \text{O}_2 = \text{SiO}_2 + 3\text{SiBr}_4
\]

The reaction takes place at temperatures over 250°C.

The reaction of hexachlorodisilane with ethyl alcohol leads to the formation, in insignificant yield, of hexaethoxydisilane (Bibl.141):

\[
\text{Si}_2\text{Cl}_6 + 6\text{C}_2\text{H}_5\text{OH} = \text{Si}_2(\text{OCH}_2\text{CH}_3)_6 + 6\text{HCl}
\]

When propyl alcohol acts on \( \text{Si}_2\text{Cl}_6 \), the principal product is tetrapropoxysilane (Bibl.119), with 12% of hexapropoxydisilane.

Under the action of organomagnesium compounds on hexachlorodisilane, it is possible to prepare hexaalkyl-(hexaaryl)-disilanes (Bibl.135):

\[
\text{Si}_2\text{Cl}_6 + 6\text{C}_4\text{H}_9\text{MgBr} = \text{Si}_2(\text{C}_4\text{H}_9)_6 + 6\text{MgClBr}
\]

Under the action of sodium on a mixture of hexachlorodisilane and an alkyl or amyl halide, tetra-substituted silanes are formed. However, when the reaction is run in two stages, the \(-\text{Si}-\text{Si}-\) bond can be preserved (Bibl.135).

\[
\text{C}_4\text{H}_9\text{Cl} + 2\text{Na} = \text{C}_4\text{H}_9\text{Na} + \text{NaCl}
\]
\[
\text{Si}_2\text{Cl}_6 + 6\text{C}_4\text{H}_9\text{Na} = \text{Si}_2(\text{C}_4\text{H}_9)_6 + 6\text{NaCl}
\]
When polyhalosilanes react with an alkali (best of all with 30% KOH), one mol of hydrogen is liberated at each -Si-Si- bond, as with the -Si-H bonds:

\[-\text{Si-Si} + 2\text{KOH} \rightarrow 2\text{Si-O}K + \text{H}_2\]

The quantitative determination of the number of -Si-Si- bonds in the polysilane molecules is based on this reaction.

The polyhalosilanes have not yet found practical application.

Table 8 gives the properties of halo-derivatives of the higher silanes:

<table>
<thead>
<tr>
<th>Physical Properties of Halo-Derivatives of the Higher Silanes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>a)</strong></td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>Hexafluorodisilane</td>
</tr>
<tr>
<td>Hexachlorodisilane</td>
</tr>
<tr>
<td>Hexabromodisilane</td>
</tr>
<tr>
<td>Hexaiododisilane</td>
</tr>
<tr>
<td>Pentachlorodisilane</td>
</tr>
<tr>
<td>Pentabromodisilane</td>
</tr>
<tr>
<td>Octachlorotrisilane</td>
</tr>
<tr>
<td>Octabromotrisilane</td>
</tr>
<tr>
<td>Decachlorotetrasilane</td>
</tr>
<tr>
<td>Decabromotetrasilane</td>
</tr>
<tr>
<td>Dodecachloropentasilane</td>
</tr>
<tr>
<td>Dodecachlorogexasilane</td>
</tr>
<tr>
<td>Dodecachlorodecasilane</td>
</tr>
</tbody>
</table>

a) Name; b) Formulas; c) Melting Point, °C; d) Boiling Point, °C;

e) Bibliography

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CHAPTER III

ORGANO-SUBSTITUTED SILANES

Hydrogen and halogen atoms and alkoxy groups in the molecules of silanes and their derivatives may be replaced by organic radicals, forming substituted silanes containing --Si-C-- bonds. The thermal and chemical stability of such compounds is considerably higher than the stability of compounds containing the --Si-H or --Si-Si-- bonds.

Organo-substituted silanes may be arranged in the following series in the order of increasing stability:

$$\text{H}_2\text{SiR} < \text{H}_2\text{SiR}_2 < \text{HSiR}_3 < \text{SiR}_4$$

Completely substituted silanes SiR₄ possess the greatest stability, and very many compounds of this type have been prepared. Compounds of the type H₃SiR or H₂SiR₂ are less stable, and in view of the difficulties in their synthesis, considerably fewer of them are known than SiR₄ compounds.

Methylsilane CH₃SiH₃ and dimethylsilane (CH₃)₂SiH₂ were synthesized in 1919 (Bibl.1), while compounds of the type R₂SiH have long been known. Thus, triethylsilane (C₂H₅)₃SiH and triphenylsilane (C₆H₅)₃SiH were synthesized as long ago as 1872 (Bibl.2), and tripropylsilane (C₃H₇)₃SiH was also synthesized in 1872 (Bibl.3). Tetraethylsilane (C₂H₅)₄Si was synthesized in 1863 (Bibl.4). Other derivatives of the SiR₄ type have been studied by many investigators. Organo-substituted di- and
trisilanes were prepared by Kipping; substituted tetra, penta and hexasilanes are unknown down to the present time.

The principal methods of preparing substituted silanes may be reduced to three types:

1. Preparation of substituted silanes by the action of various organometallic compounds on silanes, chlorosilanes, alkyl- and arylchlorosilanes.

This method has permitted the synthesis of many organo-substituted silanes. The first reactions were conducted by the action of organozinc or organomercury compounds on SiCl₄ (Bibl.5). The reaction takes place with great difficulty and requires a high temperature and prolonged heating, as a result of which this method has lost not only its practical interest but also its interest from the point of view of synthesis. Substituted silanes today are prepared by the action of organomagnesium compounds and SiX₄. The reaction between SiCl₄ and ethylmagnesium iodide was accomplished in 1904 (Bibl.6). All four possible products were obtained: ethyltrichlorosilane, diethyldichlorosilane, triethylchlorosilane, and tetraethylsilane. On reaction of ethyltrichlorosilane with phenylmagnesium bromide, ethylphenylchlorosilane was obtained and on the reaction of this compound with propylmagnesium bromide, ethylphenylpropylchlorosilane was obtained. The reaction between chlorosilane and ethylmagnesium bromide in equimolecular ratio led to the formation of ethyltrichlorosilane almost exclusively.

Kipping (Bibl.7) in 1907 used Grignard's reagent to prepare a number of mixed tetra-substituted silanes:

\[
\begin{align*}
SiCl₄ + C₄H₉MgBr &\rightarrow C₄H₉SiCl₂ + MgClBr \\
C₄H₉SiCl₂ + C₄H₉MgBr &\rightarrow C₄H₉Si + C₄H₉Cl + MgClBr \\
C₄H₉SiCl₂ + C₄H₉MgBr &\rightarrow C₄H₉Si + C₄H₉Cl + MgClBr \\
C₄H₉SiCl₂ + C₄H₉MgBr &\rightarrow C₄H₉Si + C₄H₉Cl + MgClBr
\end{align*}
\]
These reactions between SiCl$_4$ or alkyl-(aryl)-halosilanes and Grignard's reaction were accompanied by the formation of a considerable quantity of by product.

A disadvantage of this method is the need for using ether, which involves the danger of fire. I have proposed a method for conducting this reaction without ether in a medium of aromatic hydrocarbon in the presence of the ethyl ester of orthosilicic acid as a catalyst. This method has acquired practical importance (Bibl.8).

To prepare substituted silanes, the halo-derivatives of silicon, SiX$_4$, may be used, where X = Cl, Br, I, or F. The replacement of the halogen by an organic radical takes place more easily when SiBr$_4$ is used than with SiCl$_4$, but even in this case, it is very difficult to replace the fourth halogen atom, and a mixture of products of all four degrees of substitution is usually obtained.

SiF$_4$ reacts with organomagnesium compounds with more difficulty than SiCl$_4$, and when SiF$_4$ is used, tetra-substituted silanes cannot be obtained. They may be synthesized by the action of sodium silico-fluoride (Na$_2$SiF$_6$) on Grignard's reagent (Bibl.10).

The tetra-substituted silanes are easily formed by replacing the alkoxy groups by an organic radical under the action of organomagnesium compounds and alkyl- or aryl-substituted esters of orthosilicic acid. The reaction is run without using ethyl ether and at somewhat higher temperatures. This method is very simple and convenient for preparing substituted silanes containing various numbers of organic radicals (Bibl.11).

The organolithium compounds, as was first shown by K.A.Kocheshkov and V.A. Zasosov (Bibl.12) may be successfully used in the synthesis of substituted silanes of the SiR$_4$ type. The reaction takes place between alkyllithium or aryllithium and SiCl$_4$ with the complete or partial replacement of the halogens by organic radicals.
The ethyl ester (or ethylthio-ester) of orthosilicic acid reacts in ethereal solution with alkylolithium or aryllithium compounds, giving a good yield of tetra-substituted compounds (Bibl.15a).

2. Preparation of substituted silanes by the action of sodium (the Wurtz reaction) or of other metals on a mixture of alkyl or aryl halide and halosilane.

This reaction was first used by Polis in 1871, who acted on SiCl₄ with an alkyl halide and metallic sodium (Bibl.16). The reaction takes place according to the formula:

\[4RX + SiCl₄ + 8Na \rightarrow 8NaCl + Si₄R₄\]

The action of sodium on a mixture of aryl or alkyl halide and hexachlorodisilane or hexachlorodisiloxane leads to the destruction of the Si-Si and Si-O bonds and the formation of tetra-substituted silanes. The substituted disilanes and disiloxanes, such as, for instance, hexaphenyldisilane, do not react even on boiling with an excess of sodium for 10 hours (Bibl.17).

When sodium in chlorobenzene acts on hexachlorodisilane or hexachlorodisiloxane, certain quantities of tetraphenylsilane are obtained in each case, but the principal products are hexaphenyldisilane and hexaphenyldisiloxane respectively. When hexachlorodisilane reacts with sodium and benzylchloride, hexabenzylsilane is obtained. A number of tetra-substituted silanes and halosiloxanes have been prepared by this method.

The reaction between sodium, alkyl or arylhalosilanes, and halosilanes has been studied by many investigators. It has not lost interest even today, but the synthesis of the tetra-substituted silanes is more conveniently carried out with...
organomagnesium compounds (Bibl.18). Aromatic and aliphatic hydrocarbons may be used as solvents. The reagents may be various halosilanes, alkyl- and arylhalosilanes (Bibl.19). The tetra-substituted silanes may also be conveniently prepared by means of organolithium compounds (Bibl.19a).

3. Preparation of substituted silanes by the direct action of an alkyl or aryl halide on elementary silicon or on alloys of silicon with copper or other metals.

This method is important primarily in the synthesis of alkyl- and arylchlorosilanes. The reaction takes place at temperatures of 280 - 450°C; and it yields mainly alkyl- or arylchlorosilanes with a certain quantity of tetraalkyl- and tetraarylsilanes. The conditions under which tetra-substituted silanes are obtained by this method have been little studied.

**MONO-SUBSTITUTED SILANES**

Methylsilane CH₃SiH₃ has been prepared by the reaction between monochlorosilane with dimethylzinc by the vapor-phase method at low concentrations of the reagents.

\[ \text{H₃SiCl} + \text{Zn(CH₃)₂} \rightarrow \text{CH₃SiH₃} + \text{H₃ZnCl} \]

With a small excess of methylzinc, the yield of methylsilane is quantitative (without admixture of by products).

Methylsilane is a gas; melting point -156.5°C; boiling point -57°C; specific gravity 0.62 (at -57°C). It does not ignite in air, and explodes with oxygen.

Water does not act on methylsilane, but alkali cleaves it. Under proper conditions, under the action of an aqueous solution of alkali, methyltrihydroxysilane is formed:

\[ \text{CH₃SiH₃} + 3\text{H₂O} \rightarrow \text{CH₃Si(OH)₃} + 3\text{H₂} \]

and condenses into a complex polymer. The references in the literature to the formation of an acid by cleavage of water:

\[ \text{CH₃Si(OH)₃} \rightarrow \text{CH₃Si(OH)₂ + H₂O} \]
have not been confirmed by recent work.

Stock (Bibl. 20, 21) described the energetic evolution of hydrogen as a result of the action of NaOH on methyilsilane. The reaction is believed by the author to proceed as follows:

\[
\begin{align*}
\text{CH}_3\text{SiH}_2 + 2\text{H}_2\text{O} & \rightarrow \text{NaOH} \rightarrow \text{CH}_3\text{Si(OH)}_2 + 3\text{H}_2 \\
2(\text{CH}_3)\text{SiH}_2 + 2\text{H}_2\text{O} & \rightarrow \text{NaOH} \rightarrow [(\text{CH}_3)\text{SiO}]_2 + 4\text{H}_2 \\
\end{align*}
\]

In an excess of alkali, sodium silanolate is formed:

\[
[(\text{CH}_3)\text{SiO}]_2 + 2\text{NaOH} \rightarrow 2\text{H}_2\text{O} + 2(\text{CH}_3)\text{Si(ONa)}_2
\]

An interesting method of preparing mono and dialkylsilanes, based on the replacement of chlorine by hydrogen in alkylchlorosilanes, was described a few years ago.

Lithium-aluminum hydride was used as the hydrogenation agent.

Schematically the reaction proceeds as follows:

\[
\text{RSiCl}_3 + 3\text{H}_2 \rightarrow \text{RSiH}_3 + 3\text{HCl}
\]

Ethylsilane, propylsilane, butylsilane, phenylsilane, diethylsilane, and dipropylsilane were prepared by this method (Bibl. 22).

Under the action of HCl and AlCl\text{3}, methylsilane is chlorinated, with the formation of methylchlorosilane CH\text{3}SiH\text{2}Cl and methylidichlorosilane CH\text{3}SiH\text{Cl}\text{2}.

**DI-SUBSTITUTED SILANES**

Dimethylsilane (CH\text{3})\text{2}SiH\text{2}, like methylsilane, is prepared by the action of dimethylzinc on dichlorosilane, or by chlorination of methylsilane by HCl or aluminum trichloride, followed by the reaction of the product with dimethylzinc

\[
\text{CH}_3\text{SiH}_2 + \text{HCl} \rightarrow \text{CH}_3\text{SiH}_2\text{Cl} + \text{H}_2
\]
Dimethylsilane is a gas; melting point -150°C; boiling point -20°C; it is decomposed in alkaline solutions, forming a polymeric product whose elementary composition corresponds to that of dimethylsilicone.

\[(\text{CH}_3)_2\text{SiH} + \text{H}_2 \rightarrow [(\text{CH}_3)_2\text{Si}]_n + 2\text{H}_2\]

There are indications in the literature that other di-substituted silanes in the pure form could not be obtained even on repeated fractionation (Bibl.23). Diethyl- and dipropyl silane were first prepared only in 1947 (Bibl.22).

**TRI-SUBSTITUTED SILANES**

All the tri-substituted silanes are liquids or crystalline substances under ordinary conditions. The boiling points of the tri-substituted silanes are over 100°C, which facilitates their synthesis under laboratory conditions.

The tri-substituted silanes are usually prepared by the action of organozinc or organomagnesium compounds on trichlorosilane. Triethylsilane \((\text{C}_2\text{H}_5)_3\text{SiH}\) is obtained when ethylzinc reacts with tetrahexyloxy silane in the presence of sodium. Tripropylsilane has been synthesised by reacting propylzinc with trichlorosilane in a sealed tube; in this case tetrapropylsilane is also formed (Bibl.24).

\[2\text{SiHCl}_3 + 4\text{Zn(C}_2\text{H}_5\text{)}_2 \rightarrow \text{SiH(C}_2\text{H}_5\text{)}_3 + (\text{C}_2\text{H}_5)_2\text{Si} + 3\text{ZnCl}_2 + \text{Zn} + \text{C}_2\text{H}_6\]

Trialkylsilanes have been obtained by the reaction of alkyl chlorides with trichlorosilane in the presence of metallic sodium (Bibl.25).

\[\text{HSiCl}_3 + 6\text{Na} + 3\text{RCI} \rightarrow \text{HSiR}_3 + 6\text{NaCl}\]

The literature data on the synthesis of triphenylsilane and on its physical properties are very contradictory.

In one paper it is stated that triphenylsilane \((\text{C}_6\text{H}_5)_3\text{SiH}\) is obtained in the
form of crystals of melting point 200 - 203°C (Bibl.26). Kipping and Murray (Bibl.27) advanced the hypothesis that on the destructive distillation of octa-
phenylocycloctetrasilane $Si_4(C_6H_5)_8$ by them, triphenylsilane was obtained in the form
of an oily product that did not solidify at 0°C. Other investigators (Bibl.28) dispute the possibility of preparing triphenylsilane by these methods and state that
the substance obtained under the action of Grignard's reagent on trichlorosilane has
a boiling point of 152 - 167°C (at 2 mm) and crystallizes in white plates from
alcohol; melting point 36 - 37°C. These data, however, are not confirmed in the
literature.

Ladenburg (Bibl.29) heated tetraphenylsilane with an equivalent of bromine on a
water bath and then with a 10% excess of bromine for 8 - 10 hours in a sealed tube
at 150°C; as a result bromobenzene and triphenylbromosilane were formed. On further
bromination, diphenylbromosilane was obtained (Bibl.30).

On the action of alkyllithium or aryllithium on triethyilsilane, it was noted
that an alkyl or aryl radical is exchanged for hydrogen (Bibl.31).

$$(C_6H_5)_3SiH + RLi \rightarrow (C_6H_5)_3SiR + LiH$$

Triethylsilane was prepared by the action of ethylmagnesium bromide on ethyl-
dichlorosilane.

$$C_4H_9SiCl_2H + 2C_2H_5MgBr \rightarrow (C_4H_9)_3SiH + 2MgClBr$$

On the reaction of triethylsilane with an alkyllithium, triethylbutylsilane and tri-
ethylphenylsilane were obtained. Under the action of triethylsilane with sodium-
alcoholate, hydrogen is given off and triethylthoxysilane is formed.

In 1934 triethylsilane was prepared by the reaction of ethylmagnesium bromide
and trichlorosilane. (The reagents were taken in molar ratio 3 : 1.)

A method of preparing trimethylsilane by the action of trichlorosilane on
methyllumagnesium bromide has been described (Bibl.33).
Tribenzylsilane has been obtained in low yield by reacting sodium with tribenzylchlorosilane (Bibl.34, 35) and the possible mechanism of this reaction is as follows:

\[
\begin{align*}
(C_6H_5CH_3)_3SiCl + 2Na & \rightarrow (C_6H_5CH_3)_3SiNa + NaCl \\
(C_6H_5CH_3)_3SiNa + H_2O & \rightarrow NaOH + (C_6H_5CH_3)_3SiH
\end{align*}
\]

Tribenzylsilane in presence of a solution of KOH in acetone is oxidized to hexabenzylidisiloxane:

\[
2(C_6H_5CH_3)_3SiH + O_2 \rightarrow H_2 + [(C_6H_5CH_3)_2Si]_2
\]

Triphenylsilane has been prepared in 73% yield by the action of phenylmagnesium bromide on trichlorosilane. When triphenylsilane reacts with metallic sodium in liquid ammonia, hexaphenylaminodisilane is formed, which is stable to boiling NaOH. HCl cleaves this amine, forming triphenylhydroxysilane and ammonium chloride. It was found that bromine reacts quantitatively with triphenylsilane to form triphenylbromosilane and HBr (Bibl.36, 37).

The trialkylsilanes are liquids, insoluble in water and soluble in many organic solvents. They may be distilled without decomposition. The hydrogen in their molecules is readily replaced by bromine. The bromides so obtained are saponified by water, forming the corresponding hydroxysilanes:

\[
\begin{align*}
(C_6H_5)_3SiH + Br_2 & \rightarrow (C_6H_5)_3SiBr + HBr \\
(C_6H_5)_3SiBr + H_2O & \rightarrow (C_6H_5)_3SiOH + HBr
\end{align*}
\]

The principal properties of a few mono, di, and tri-substituted silanes are given in Tables 9 and 10.
Table 9

Physical Properties of Mono, Di, and Tri-Substituted Organosilanes

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c)</th>
<th>d)</th>
<th>e)</th>
<th>f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylsilane</td>
<td>(CH₃)₂SiH</td>
<td>156.5</td>
<td>57</td>
<td>0.64</td>
<td>1.33</td>
</tr>
<tr>
<td>Diethylsilane</td>
<td>(CH₃)₂SiH₂</td>
<td>150</td>
<td>20</td>
<td>1.33</td>
<td></td>
</tr>
<tr>
<td>Trimethylsilane</td>
<td>(CH₃)₃SiH</td>
<td>135.8</td>
<td>6.7</td>
<td>134</td>
<td></td>
</tr>
<tr>
<td>Ethylsilane</td>
<td>(CH₃)₂SiH</td>
<td>179.7</td>
<td>13.7</td>
<td>134</td>
<td></td>
</tr>
<tr>
<td>Dimethylsilane</td>
<td>(CH₃)₂SiH₂</td>
<td>134</td>
<td>55.9</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>Triethylsilane</td>
<td>(CH₃)₃SiH</td>
<td>156.9</td>
<td>108.7</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>Tripropylsilane</td>
<td>(C₃H₇)₂SiH</td>
<td>170</td>
<td>24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isobutylsilane</td>
<td>(CH₃)₂CH₂SiH</td>
<td>138.2</td>
<td>26.1</td>
<td>134</td>
<td></td>
</tr>
<tr>
<td>Triisobutylsilane</td>
<td>[(CH₃)₂CH₂]₃SiH</td>
<td>246</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triallylsilane</td>
<td>(CH₂)₃SiH</td>
<td>246</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triphenylsilane</td>
<td>(C₆H₅)₂SiH</td>
<td>36</td>
<td>37</td>
<td>26.27</td>
<td></td>
</tr>
<tr>
<td>Dicyclohexylsilane</td>
<td>(C₆H₁₀)₂SiH</td>
<td>36</td>
<td>37</td>
<td>26.27</td>
<td></td>
</tr>
<tr>
<td>Tribenzylsilane</td>
<td>(C₆H₅)₃SiH</td>
<td>180</td>
<td>185</td>
<td>135</td>
<td></td>
</tr>
<tr>
<td>Tri-α-naphthyilsilane</td>
<td>(C₆H₅)₂CH₂SiH</td>
<td>49</td>
<td>16.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tri-phenylsilane</td>
<td>(C₆H₅)₂SiH₂</td>
<td>240</td>
<td>92</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Melting Point, °C; d) Boiling Point, °C; e) Specific Gravity, d₂⁰; f) Bibliography

Table 10

Physical Properties of Organosilanes with Unsaturated Radicals

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c)</th>
<th>d)</th>
<th>e)</th>
<th>f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinylsilane</td>
<td>CH₂=C=CH-SiH</td>
<td>-22.8</td>
<td>0.7630</td>
<td>1.4430</td>
<td>99</td>
</tr>
<tr>
<td>Diisobutylsilane</td>
<td>(CH₂=CH₂CH₂)₂SiH</td>
<td>122.5</td>
<td>0.7630</td>
<td>1.4430</td>
<td>99</td>
</tr>
<tr>
<td>Triallylsilane</td>
<td>(CH₂=CH₂CH₂)₃SiH</td>
<td>61.6</td>
<td>1.4678</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allyl-(8-methyl-4-penteny) methysilane</td>
<td>CH₃-C=cH₂CH₂</td>
<td>183.4</td>
<td>0.7881</td>
<td>1.1482</td>
<td>99</td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Boiling Point, °C; d) Specific Gravity, d₂⁰; e) Index of Refraction, nD⁰; f) Bibliography
TETRA-SUBSTITUTED SILANES

The tetra-substituted silanes are prepared with comparative ease. Their stability depends on the molecular weight of the radicals attached to the silicon as well as on the symmetry of the molecules. Among the substituted silanes, the tetra-substituted silanes are most stable.

The hydrogen atom in silanes may be replaced by either like or unlike radicals. When the hydrogen atoms in silane are replaced by like radicals, simple tetra-substituted silanes are formed, while when they are replaced by unlike radicals, mixed tetra-substituted silanes are formed. The latter are an extensive group of organosilicon compounds, and a special section of this Chapter will be devoted to them.

Simple Tetra-Substituted Silanes

Methods of Preparation

The most widely used method of preparing simple tetra-substituted silane is the method of replacing the chlorine in $\text{SiCl}_4$. Friedel and Crafts (Bibl.38) prepared tetraethylsilane by the action of ethylzinc on $\text{SiCl}_4$ in a sealed tube:

$$\text{SiCl}_4 + 2\text{Zn}(\text{C}_2\text{H}_5)_2 \rightarrow \text{Si}((\text{C}_2\text{H}_5)_2)_4 + 2\text{ZnCl}_2$$

When $\text{SiCl}_4$ reacts with phenylbromide or chloride in an ethereal solution in presence of sodium, a tetraarylsilane is obtained (Bibl.39):

$$\text{SiCl}_4 + 4\text{RCI} + 8\text{Na} \rightarrow \text{SiR}_4 + 8\text{NaCl}$$

This reaction sometimes proceeds very violently, and then cooling is necessary. In all cases $\text{R}_3\text{SiCl}$ and other alkyl-(aryl)-chlorosilanes are formed as by products. This method has made it possible to prepare a large number of different tetra-substituted silanes, but in low yields.
A large number of different tetra-substituted silanes have been prepared by using the Grignard reaction. The reactions between SiCl₄ and organomagnesium compounds were conducted in ethereal solution:

\[
\text{SiCl}_4 + 4\text{RMgCl} \rightarrow \text{SiR}_4 + 4\text{MgCl}_2
\]

The product so formed was decomposed under the action of water, the ether was driven off, and the residue was treated with concentrated sulfuric acid; the SiR₄ does not dissolve in the acid and can be easily separated.

By using the Grignard reaction without ethyl ether, considerable quantities of tetra-substituted silanes as well as triarylsiloxysilanes can be obtained, in addition to the di- and tri-substituted silanes.

With the object of elucidating the relative activity of various organomagnesium compounds (Bibl.41) on their reaction with alkylchlorosilanes, the reactions between mixtures of various organomagnesium compounds and trialkylchlorosilanes were investigated.

On the reaction of a mixture of various molar quantities of methylmagnesium bromide and ethylmagnesium bromide with trichlorosilane, only methyltrimethylsilane is formed.

\[
\text{CH}_3\text{MgBr} + \text{C}_2\text{H}_5\text{MgBr} + \text{C}_3\text{H}_5\text{SiCl} \rightarrow \text{(CH}_3\text{)}_3\text{SiCl} + \text{MgCl}_2 + \text{C}_2\text{H}_5\text{MgCl}
\]

When a mixture of equal molar quantities of trimethylchlorosilane and triethyl-chlorosilane reacts with ethylmagnesium bromide, ethyltrimethylsilane and tetraethylsilane are formed in the molar ratio of about 2 : 1.
When mixtures of equal molar quantities of trimethylchlorosilane and triethylchlorosilane react with propylmagnesium bromide, the reaction proceeds toward the formation of propyltrimethylsilane, while propyltriethylsilane is not formed.

\[ (CH_3)_3SiCl + (C_2H_5)_3SiCl + C_4H_9MgBr \rightarrow (CH_3)_3SiC_4H_9 + (C_2H_5)_3Si + MgClBr \]

Reaction of triethylchlorosilane with a mixture of ethyl- and methylmagnesium bromides. In a three-liter three-necked flask, provided with a stirrer with a mercury seal, a reflux condenser, and a dropping funnel, 139 ml (0.42 mol) of methylmagnesium bromide and 165 ml (0.42 mol) of ethylmagnesium bromide are placed. To this mixture 63 g (0.42 mol) of triethylchlorosilane are added during 15 minutes, under stirring and cooling.

The mixture is boiled 4 hours; then the reflux condenser is replaced by a straight condenser, and a liquid is distilled from the reaction flask at temperatures up to 100 - 110°C. The process of distillation lasts 8 hours. The distillate so obtained is again returned to the reaction flask, and, with stirring, 500 ml of water is slowly added to decompose the unreacted Grignard reagent. The reaction product is then distilled with steam. The organic layer is separated, while the water layer is extracted with 65 ml of ethyl ether. The ether extract is combined with the separated layer, the ether is distilled off, and the residue is boiled with dilute HCl for 8 hours to transform possible traces of triethylhydroxysilane (formed by hydrolysis of the unreacted triethylchlorosilane) into hexaethyldisiloxane.

The organic layer is then separated, washed with water, and dried over anhydrous magnesium sulfate. The fractionation of the product in a column with 20 theoretical plates yields 36.1 g (0.28 mol) of methyltriethylsilane; boiling point 126°C (729 mm); index of refraction nD^20 = 1.4160. Tetraethylsilane was not obtained.

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Reaction of ethylmagnesium bromide and a mixture of trimethylchlorosilane and triethylchlorosilane. To 0.5 mol of ethylmagnesium bromide a mixture of 0.5 mol each of trimethylchlorosilane and triethylchlorosilane is added. The further treatment is the same as described above. The fractionation of the reaction product gave 18.3 g (0.18 mols) of ethyltrimethylsilane, boiling point 62°C (734 mm); index of refraction \( n_D^{20} = 1.3819 - 1.3821 \). On distillation 13.6 g (0.095 mols) of tetraethylsilane was also obtained; boiling point 152 - 156°C (734 mm); index of refraction \( n_D^{20} = 1.4104 \); and 25.1 g (0.101 mol) of hexaethylsiloxane; boiling point 128°C (30 mm); index of refraction \( n_D^{20} = 1.4335 \).

Reaction of propylmagnesium bromide with a mixture of trimethylchlorosilane and triethylchlorosilane. To 0.5 mol of propylmagnesium bromide a mixture of 0.5 mol each of trimethylchlorosilane and triethylchlorosilane is added. The further treatment is conducted as described above, but, before fractionating, the reaction product is treated with 50 ml of cold concentrated sulfuric acid which, as is well known, dissolves hexaalkyldisiloxanes and does not dissolve tetraalkylsilanes. The upper layer formed on treatment with \( \text{H}_2\text{SO}_4 \) is separated, and, after the acid is washed out with water and a solution of sodium bicarbonate, it is then dried over anhydrous sodium sulfate. Fractionation of this upper layer gave 33.3 g (0.287 mol) of propyltrimethylsilane; boiling point 89°C (729 mm), index of refraction \( n_D^{20} = 1.4330 \). In this layer 22.1 g of a product with index of refraction \( n_D^{20} = 1.404 \) was also found. No propylethylsilane was found. The sulfuric acid layer was treated with ice water; the organic layer separated was removed, washed with water, dried with sodium sulfate, and fractionated. It yielded 9.5 g of 1, 1, 1-trimethyl-3, 3, 3-triethylsiloxane; boiling point 80° (30 mm); index of refraction \( n_D^{20} = 1.4105 \); and 10 g of hexaethylsiloxane; boiling point 137°C (29 mm); index of refraction \( n_D^{20} = 1.4332 \).

Tetra-substituted silanes are obtained in better yields and with smaller quantities of by products when Grignard's reagent acts on trialkylchlorosilanes than
when it acts on alkyl trichlorosilanes (Bibl.42).

Z. M. Manulkin (Bibl.43) has prepared tetraethylsilane by the action of ethylmagnesium bromide on sodium fluosilicate.

Many methods of preparing Si$R_4$ from the esters of orthosilicic acid by replacing the alkoxy groups are known. This reaction was first performed by heating alkylzinc and an ester of orthosilicic acid in a sealed tube in the presence of sodium (Bibl.44).

\[
\text{Si}(\text{OC}_2\text{H}_5)_4 + 2\text{Zn}(\text{C}_6\text{H}_5)_2 \xrightarrow{\text{Na}} \text{Si}(\text{C}_6\text{H}_5)_4 + 2\text{Zn}(\text{OC}_2\text{H}_5)_2
\]

The tetra-substituted silanes were also obtained by the action of organomagnesium compounds on esters of orthosilicic acid:

\[
\text{Si}(\text{OC}_2\text{H}_5)_4 + 4\text{RMgBr} \xrightarrow{} \text{Si}R_4 + 4\text{Mg}(\text{OC}_2\text{H}_5)_2
\]

Mono- and di- substituted esters of orthosilicic acid may also be converted into Si$R_4$ by heating with acid chlorides (CH$_3$COCl, C$_6$H$_5$COCl) followed by the action of a Grignard reagent on the chlorosilane so formed (Bibl.45):

\[
\begin{align*}
\text{(C}_3\text{H}_5)_2\text{Si}(\text{OC}_2\text{H}_5)_2 + 2\text{C}_6\text{H}_5\text{COCl} & \xrightarrow{} \text{(C}_3\text{H}_5)_2\text{SiCl}_2 + 2\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5 \\
\text{(C}_6\text{H}_5)_3\text{SiCl}_2 + 2\text{C}_6\text{H}_5\text{MgCl} & \xrightarrow{} \text{(C}_6\text{H}_5)_4\text{Si} + 2\text{MgCl}_2
\end{align*}
\]

Simple tetra-substituted silanes are formed when mixed tetra-substituted silanes are heated; for instance, by heating triethylphenylsilane, tetraethylsilane may be obtained:

\[
2\text{(C}_3\text{H}_5)_3\text{SiC}_6\text{H}_5 \xrightarrow{} \text{(C}_3\text{H}_5)_3\text{Si} + (\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_6\text{H}_5)_2
\]

Dolgov (Bibl.46) effected this reaction in a hydrogen atmosphere at 260°C and 100 atm pressure.

Soshestvenskaya has described an interesting method of preparing tetrabenzyl-
silane by the action of Grignard's reagent on \( \text{Na}_2\text{SiF}_6 \) (Bibl.47). When an ether solution of benzylmagnesium bromide acts on \( \text{Na}_2\text{SiF}_6 \) at room temperature, the reaction makes practically no progress even over a period of 21 days. Heating a mixture of \( \text{Na}_2\text{SiF}_6 \) with the Grignard reagent (after distilling off the ether from it) for one hour to 160 - 170°C leads to the formation of tetrabenzylsilane:

\[
\text{Na}_2\text{SiF}_6 + 4\text{C}_6\text{H}_5\text{CH}_3\text{MgCl} \rightarrow (\text{C}_6\text{H}_5\text{CH}_3)_4\text{Si} + 2\text{NaCl} + 2\text{MgF}_2 + 2\text{MgCl}_2
\]

The yield of tetrabenzylsilane is over 20.7% figured on the basis of the \( \text{Na}_2\text{SiF}_6 \) taken. No tribenzylfluorosilane was obtained in this case.

Tetrabenzylsilane crystallizes in coarse colorless prisms, melting point \( 127.5^\circ\text{C} \).

It is possible that a longer heating time and still higher temperatures might have an effect on the yield of tetrabenzylsilane.

Tetrabutylsilane was prepared from the ethyl ester of orthosilicic acid (in 25% excess) and butylimagnesium bromide; the reaction liquid was found to heat up strongly (Bibl.45). The yield was 50%.

To prepare certain tetra-substituted silanes, organolithium compounds are used. The ethyl ester of orthosilicic acid or \( \text{SiCl}_4 \) reacts with a lithium alkyl or aryl in ether almost immediately:

\[
\text{Si(OCH}_3)_4 + 4\text{RLi} \rightarrow \text{SiR}_4 + 4\text{LiOCH}_3
\]

The yields of compounds of the \( \text{SiR}_4 \) type are high. K.Kochevskov and V.Zasosov (Bibl.48) prepared tetraphenylsilane by the reaction of phenyllithium and \( \text{SiCl}_4 \) in absolute ether.

**Reaction of phenyllithium and silicon tetrachloride.** Into a solution of phenyllithium prepared from 20.7g (0.132 mol) of bromobenzene, 2.01 g of lithium (0.29 gram-atom + 10%) and 80 cm³ of absolute ether, 3.4 g (0.02 mol) of \( \text{SiCl}_4 \) dissolved in 10 cm³ of petroleum ether was added in small portions from a dropping
funnel. The mixture was heated 2 hours on a water bath, and, after cooling, was poured into 250 cm$^3$ of ice water. The product separated and aspirated, washed with alcohol and ether and dried in the air. Yield 6.54 g (97.5% of theoretical). Melting point after one crystallization from amyl acetate, 233 - 234°C. According to Polis (Bibl.49), the melting point of tetraphenylsilane may be as high as 234°C.

A few aliphatic compounds of the SiR$_4$ type were subsequently prepared by this method (Bibl.50); [Si(OR)$_4$ may also be taken as the starting compound]. If tertiary or secondary radicals are attached to the lithium, then the chlorine atoms in SiCl$_4$ are incompletely substituted (Bibl.51).

Physical Properties

The simple tetraalkysilanes are liquids with an odor of kerosene with an admixture of turpentine; they are insoluble in water; and neither acids nor alkalies act on them. The specific gravity of the tetraalkysilanes is less than unity. Their boiling points are higher than those of the corresponding hydrocarbons; they distill without decomposition at atmospheric pressure. In presence of oxygen and on contact with an open flame, the vapors of the tetraalkysilanes explode.

The tetraarylsilanes are solid crystalline substances, very stable on heating to high temperatures. They are readily soluble in benzene and other aromatic hydrocarbons; and almost insoluble in ether and bensine.

The tetraalkyl- and tetraarylsilanes are thermally stable substances, and there are a number of properties that remind one of methane derivatives. A comparison of the physical properties of the tetraalkysilanes with the properties of the corresponding paraffin hydrocarbons showed that the boiling point, index of refraction, and density are higher in the tetraalkysilanes, while the viscosity is lower, than in the hydrocarbons.

A number of papers have been devoted to the study of the physical properties of tetraalkyl- and tetraphenylsilanes. The specific heats (Bibl.53), melting points (Bibl.54), and boiling points (Bibl.55), have been determined, and the Raman
spectrum (Bibl.56), the normal vibrations of the molecules (Bibl.57), the free rotation of the molecules (Bibl.58), the viscosity, atomic and molecular refraction (Bibl.59), have been studied. The entropy has been calculated from Kinney’s equation, and an investigation of the tetra-substituted silanes in the infrared spectrum has been made.

On ultraviolet irradiation, tetraphenylsilane and tetra-p-tolylsilane show a bright green phosphorescence. Tetra-p-diphenylsilane does not manifest this (Bibl.61). The molecular structures of tetramethysilane, hexamethyldisilane (Bibl.62), and tetrphenylsilane have also been investigated, as well as the crystallographic properties of octaphenylcycloctrasilane (Bibl.63), and the structure of hexadecamethylcyclooctasiloxane (Bibl.64).

In papers devoted to the preparation and study of the properties of tetra-substituted silanes with a double bond between the carbon atoms in the radical, the physical constants of a large number of individual compounds have been determined, such as triethylvinylsilane (Bibl.65), tetraallylsilane (Bibl.66), ethylallylisobutylbenzylsilane (Bibl.67), triethylvinylsilane, triethoxyallylsilane (Bibl.68), and other unsaturated compounds of more complex structure (Bibl.69).

Table 11 gives the physical properties of simple tetra-substituted silanes.

### Table 11

<table>
<thead>
<tr>
<th></th>
<th>A)</th>
<th>B)</th>
<th>C)</th>
<th>D)</th>
<th>E)</th>
<th>F)</th>
<th>G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetramethylsilane</td>
<td>(CH₃)₄Si</td>
<td>—</td>
<td>26,5</td>
<td>0,646</td>
<td>1,3476</td>
<td>69,78:137</td>
<td></td>
</tr>
<tr>
<td>Tetraethyilsilane</td>
<td>(C₂H₅)₄Si</td>
<td>—</td>
<td>153</td>
<td>0,7862</td>
<td>1,424</td>
<td>69,91</td>
<td></td>
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<tr>
<td>Tetrapropylsilane</td>
<td>(C₃H₇)₄Si</td>
<td>—</td>
<td>213</td>
<td>0,785</td>
<td>—</td>
<td>24,52</td>
<td></td>
</tr>
<tr>
<td>Tetrabutylsilane</td>
<td>(C₄H₉)₄Si</td>
<td>—</td>
<td>157</td>
<td>0,8008</td>
<td>1,4465</td>
<td>135:138</td>
<td></td>
</tr>
</tbody>
</table>

(continued)
<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c)</th>
<th>d)</th>
<th>e)</th>
<th>f)</th>
<th>g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetraamylsilane</td>
<td>(C₆H₁₃)₄Si</td>
<td>—</td>
<td>275</td>
<td>—</td>
<td>—</td>
<td>25</td>
</tr>
<tr>
<td>Tetraethylsilane</td>
<td>(C₄H₉)₄Si</td>
<td>231</td>
<td>0.8052</td>
<td>1.4510</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>Tetrabenzylsilane</td>
<td>(C₆H₅CH₃)₄Si</td>
<td>128</td>
<td>550</td>
<td>1.078</td>
<td>—</td>
<td>18.17, 18</td>
</tr>
<tr>
<td>Tetra-m-tolysilane</td>
<td>(C₆H₅CH₃)₄Si</td>
<td>151</td>
<td>—</td>
<td>1.118</td>
<td>—</td>
<td>16</td>
</tr>
<tr>
<td>Tetra-p-tolysilane</td>
<td>(C₆H₅CH₃)₄Si</td>
<td>228</td>
<td>—</td>
<td>1.079</td>
<td>—</td>
<td>16</td>
</tr>
<tr>
<td>Tetradiphenylsilane</td>
<td>(C₆H₅)₄Si</td>
<td>274</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>17</td>
</tr>
</tbody>
</table>

*Cf. also Table 13 (page 178).

a) Name; b) Formula; c) Melting Point, °C; d) Boiling Point, °C;

e) Specific Gravity, d₂⁰; f) Refractive Index n₂⁰; g) Bibliography

Chemical Properties

The pyrolysis of tetraalkylsilanes has been studied in detail. For tetraethylsilane and tetrapropylsilane, the following mechanism of their cleavage is given:

\[
\begin{align*}
\text{Si(C₄H₉)₄} & \rightarrow \text{Si} + 4\text{C₄H₉} \\
\text{Si(C₄H₉)₄} & \rightarrow \text{-Si(C₄H₉)₃} + \text{C₄H₉} \quad (\text{slowly}) \\
\text{Si(C₂H₅)₄} & \rightarrow \text{Si} + 3\text{C₂H₅} \quad (\text{rapidly}) \\
\text{Si(C₃H₇)₄} & \rightarrow \text{Si(C₃H₇)₃} + \text{C₃H₇} \quad (\text{slowly}) \\
\text{Si(C₂H₅)₄} & \rightarrow \text{Si} + 3\text{C₂H₅} \quad (\text{rapidly}) 
\end{align*}
\]

Thus the cleavage of tetraethyl- and tetrapropylsilane takes place in stages with formation of silica, hydrogen, and hydrocarbons. The decomposition of tetra-substituted silanes into \(-\text{SiR}_3\) and \(\text{R}^-\) radicals takes place more slowly than the cleavage of \(-\text{SiR}_3\) into silicon and a free radical.

Ipat'yev and Dolgov (Bibl.71) have heated tetraethylsilane with hydrogen under pressure at 350°C, and have obtained ethane and triethylsilane. From phenyltrimethylsilane, under these conditions, benzene and triethylsilane were obtained.

\[
\text{Si(C₃H₇)₄} + \text{H}_2 \rightarrow \text{C₂H₆} + (\text{C₃H₇})₃\text{SiH}
\]
It was found that tetraphenylsilane is stable at 450°C; at a higher temperature it condenses to form a high-molecular substance.

In 1931 Dolgov and Vol'nov (Bibl.72) published further studies of the ability of tetra-substituted silanes to undergo disproportionation. Tetrabenzylsilane at 400°C under pressure of 100 atm, gives no reaction with hydrogen (Bibl.71). They considered the low reactivity of this compound to be due to the fact that the silicon prevents the reaction. On studying the behavior of the corresponding hydroxyl derivatives it was found that while triphenylcarbinol is easily reduced to triphenylmethane, triphenylsilanol is not reduced but is dehydrated to the dimer.

When mixtures of various quantities of tetraethylsilane and tetrapropylsilane are heated, a mixture of the following composition is formed (Bibl.72):

<table>
<thead>
<tr>
<th>Compound</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(C₆H₅)₄</td>
<td>5</td>
</tr>
<tr>
<td>C₆H₅Si(C₆H₅)₂</td>
<td>21</td>
</tr>
<tr>
<td>(C₆H₅)₂Si(C₆H₅)₃</td>
<td>40</td>
</tr>
<tr>
<td>C₆H₅Si(C₆H₅)₄</td>
<td>24</td>
</tr>
<tr>
<td>Si(C₆H₅)₆</td>
<td>10</td>
</tr>
</tbody>
</table>

L.G.Makarova and A.N.Nesmeyanov (Bibl.73) have found that tetraphenylsilane does not react with nitrogen oxides. An attempt to effect the reaction between silver nitrate and tetraphenylsilane also proved unsuccessful (Bibl.74). Tetramethylsilane was found to be very stable to heating. Its thermal decomposition begins in the range 659 - 717°C (at 850 mm) (Bibl.75).

The tetraalkylsilanes are chlorinated and brominated with relative ease. Chlorination takes place in the cold, while bromination requires heating. The halogen replaces hydrogen in the organic radical:

\[(C₆H₅)₄SiC₆H₅ + Cl₂ \rightarrow (C₆H₅)₃Si(C₆H₅Cl) + HCl\]
Friedel and Ladenburg (Bibl.76) obtained triethylchloroethylsilane and triethylidichloroethylsilane by the chlorination of tetraethylsilane.

Ushakov and Itenberg (Bibl.77) described the chlorination of tetraethylsilane, with 1 - 2% of PCl₅ used as a catalyst. Triethyl-β-chloroethylsilane, triethyl-α-chloroethylsilane and other silane derivatives were obtained in 75% yield.

**Chlorination of tetramethylsilane (Bibl.78).** Tetramethylsilane is dissolved in carbon tetrachloride, phosphorus pentachloride is added as a catalyst, and chlorine at the rate of 0.5 mol per hour is passed for four hours. During the chlorination, the system is irradiated with a 450 watt quartz lamp. About two-thirds of the product consists of polychlorinated compound, and only one-third of chloromethyltrimethylsilane.

Halogens act differently on a tetraarylsilane. Bromine, for instance, replaces one aryl radical during the course of 12 days, even in the cold:

\[(C₆H₅)₄SiC₆H₄ + Br₂ → (C₆H₅)₃SiBr + C₆H₄Br\]

PCl₅ at 180°C chlorinates a tetraarylsilane, also splitting off an aryl radical:

\[(C₆H₅)₄Si + PCl₅ → (C₆H₅)₃SiCl + (C₆H₅)Cl + PCl₃\]

\[(C₆H₅)₄Si + 2PCl₅ → (C₆H₅)₃SiCl₂ + 2(C₆H₅)Cl + 2PCl₃\]

In this way, complete cleavage of all the aryl radicals may be accomplished and SiCl₄ obtained. By hydrolysis of the halosilane so formed, all the hydroxysilanes may be obtained.
The tetraalkyl- and tetraaryl-silanes are readily chlorinated by molecular chlorine; which replaces the hydrogen in the radical, but replacement of the radical itself does not take place.

The tetraarylsilanes are nitrated under mild conditions (in CCl₄); and in this way nitro-compounds are obtained; thus, from tetraphenylsilane, Si(C₆H₄NO₄)₂ is formed (Bibl.79). Concentrated nitric acid on heating oxidizes SiAr₄. A study of the nitration product showed that the meta and para nitro-isomers were mainly formed; the ortho isomer was not found (Bibl.80). On heating in an acid medium (HCl or acetic acid) traces of the decomposition of tetraphenylsilane into benzene and triphenylhydroxysilane are detected:

\[(C₆H₄)₄Si + H₂O \rightarrow (C₆H₄)₃SiOH + C₆H₆\]

The nitro-derivatives may be reduced to amino compounds by the action of tin and HCl. The m-aminophenylsilanes are stable against the action of hot alkalies and hot HCl. The p-aminophenylsilanes are less stable, and when boiled with HCl or alkalies they are decomposed, forming alkyl- or arylsilanes and aniline (Bibl.81). The degree of stability of the o-aminophenylsilanes has not yet been studied.

Triphenylsilane does not react with lithium p-thiocresolate, nor with phenylmagnesium bromide, even after prolonged boiling of the reaction mixture (24 – 30 hours).

The preparation of other substituted silanes by using organolithium compounds has also been described (Bibl.82). At room temperature, triethylsilane was prepared...
by the Grignard reaction, and the product was then subjected to the action of butyl-
lithium. As a result, triethylbutylsilane was obtained in 58% yield. When the

---

The introduction of alkyl and aryl groups in trialkylsilanes by the aid of
organolithium compounds is conducted in ethyl ether. Petroleum ether slows down the
reaction. In the presence of lithium ethoxide, triethylsilane and ethanol form

---

When phenyllithium reacts with SiCl₄, followed by hydrolysis, triphenylhydroxy-
silane in 97% yield is formed.

\[
\text{SiCl}_4 + 3\text{C}_6\text{H}_5\text{Li} \rightarrow 3\text{LiCl} + (\text{C}_6\text{H}_5)_3\text{SiCl} + \text{H}_2\text{O} \rightarrow (\text{C}_6\text{H}_5)_3\text{SiOCl} + \text{HCl}
\]

When 3 mols of phenyllithium reacts with 1 mol of SiCl₄, and 1 mol of

---

A.D. Petrov and his associates (Bibl.83) studied the possibility of synthesizing
the asymmetric alkyl-(aryl)-silanes with aryl radicals from aromatic hydrocarbons
with condensed rings. They found that on the action of α-naphthyltriethoxysilane on

---

Under the action of hexylmagnesium bromide, the yield of α-naphthyltriethyl-
silane decreases to 45%. Under the action of methylmagnesium chloride on

---

F-TS-9191/V
Mixed Tetra-Substituted Silanes

The mixed tetra-substituted silanes are substitution products formed by the replacement of the hydrogen atoms in \( \text{SiH}_4 \) by unlike organic radicals. A study of the mixed tetra-substituted silanes made it possible to establish a number of regularities, allowing determination of the character of the bonds in molecules of the type \( \text{RSiR'}_2 \), \( \text{R}_2\text{SiR'}_2 \), \( \text{SiRR'R'R''} \), and the dependence of the physical properties on the nature of the substituent, the molecular weight, the symmetry of the radicals, etc.

Methods of Preparation

The simplest method of preparing mixed tetra-substituted silanes is based on the reaction between \( \text{SiCl}_4 \) or organochlorosilanes, or esters of orthosilicic acid or substituted ortho esters with an alkylzinc or Grignard reagent. These reactions have already been discussed in part, above.

The action of ethylzinc (Bibl.84) on phenyltrichlorosilane forms phenyltrichlorosilane

\[
2\text{C}_6\text{H}_5\text{SiCl}_3 + 3\text{Zn(C}_2\text{H}_5)_2 \rightarrow 2\text{C}_6\text{H}_5\text{Si(C}_2\text{H}_5)_3 + 3\text{ZnCl}_2
\]

At the same time, as a result of rearrangement, tetraphenylsiline and diphenyl-diethylsilane were also obtained:

\[
2\text{C}_6\text{H}_5\text{Si(C}_2\text{H}_5)_3 \rightarrow (\text{C}_6\text{H}_5\text{Si})_2 : (\text{C}_6\text{H}_5\text{Si})(\text{C}_2\text{H}_5)_2
\]

Dolgov and Vol'nov state that under the action of diethylzinc on triphenylchlorosilane at \( 230^\circ\text{C} \), not only triphenylethylsilane, but also a certain quantity of diethylphenylsilane and tetraethylsilane are formed.

On the reaction between organozinc compounds and various esters of orthosilicic acid, the successive replacement of the alkoxy groups takes place (Bibl.85).

\[
2(\text{CH}_3\text{O})_2\text{Si} + \text{Zn(C}_2\text{H}_5)_2 + 2\text{Na} \rightarrow 2\text{C}_6\text{H}_5\text{Si(OC}_2\text{H}_5)_3 + 2\text{CH}_3\text{OHNa} + \text{Zn}
\]
Under the action of nitric acid (at room temperature, in a solvent) on tetra-substituted silanes containing aromatic radicals, the aromatic radicals are nitrated.

The difficulty of nitration increases in the following order: phenyltriethylsilane, diphenyldiethylsilane, and tetraphenylsilane (Bibl.86). When these compounds are nitrated, the nitro group goes into the para or meta position with respect to the silicon atom. We give the quantitative relations between the isomers obtained on nitration of these substances.

<table>
<thead>
<tr>
<th>Yield of Para- nitro- Isomer, %</th>
<th>Yield of meta- Nitro- Isomer, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₅Si(C₂H₅)₃ ..........................</td>
<td>83 ..........................</td>
</tr>
<tr>
<td>(C₆H₅)₂Si(C₂H₅)₂ ........................</td>
<td>70 ..........................</td>
</tr>
<tr>
<td>(C₆H₅)₃SiC₂H₅ ..........................</td>
<td>40 ..........................</td>
</tr>
<tr>
<td>(C₆H₅)₄Si ...............................</td>
<td>24 ..........................</td>
</tr>
</tbody>
</table>

The conclusion may be drawn from these data that the triethylsilane group (C₂H₅)₃Si is mainly oriented toward the para position, and the triphenylsilane group (C₆H₅)₃Si toward the meta position.

A large number of mixed tetra-substituted silanes have been prepared by the Grignard reaction (Bibl.87).
\[ C_8H_{16}SiCl_3 + 3CH_3MgBr \rightarrow C_8H_{16}Si(CH_3)_3 + 3MgClBr \]
\[ (C_8H_{16})_2SiCl_2 + 2CH_3MgBr \rightarrow (C_8H_{16})_2Si(CH_3)_2 + 2MgClBr \]

The radicals in the mixed tetra-substituted silanes may be made more complex by replacing the halogen atoms in them by organic radicals (Bibl.88).

\[ \begin{align*}
BrC_6H_5 & \rightarrow C_6H_5CH_3 \\
C_6H_5Si & \rightarrow C_6H_5CH_3 \\
C_6H_5 & \rightarrow C_6H_5CH_3
\end{align*} \]

The literature describes methods of preparing alkyltrimethylsilanes and alkyltrihethylsilanes, in which the alkyl radical has a high molecular weight, and also describes their properties. Under the action of a Grignard reagent on SiCl₄, alkyltrichlorosilanes were at first obtained. The products, after being purified by fractional distillation, were introduced into an ether solution of methylmagnesium bromide or ethylmagnesium bromide, and as a result alkyltrimethylsilanes or alkyltrihethylsilanes respectively, in yield of about 70% of theoretical, were obtained.

\[ R\text{MgBr} + SiCl_3 \rightarrow RSiCl_3 + MgCl_2 \]
\[ RSiCl_3 + 3CH_3MgBr \rightarrow RSi(CH_3)_2 + 3MgCl_2 \]

Such yields are obtained, for instance, in the synthesis of lauryltrimethylsilane and hetnyltrimethylsilane by the reaction between trimethylchlorosilane and the corresponding Grignard reagent.

When methyllithium reacts with triethylsilane (Bibl.89), methyltriethylsilane is formed:

\[ (C_6H_{15})_3SiH + LiH \rightarrow (C_6H_{15})_3SiH \cdot LiH \]

Triphenylsilane reacts with organolithium compounds to form the corresponding tetra-substituted silanes (Bibl.90):
To perform the reaction, one equivalent of an ether solution of the organo-
lithium compound is added to a solution of triphenylsilane in ethyl ether. After
the completion of the reaction, the mixture is treated with water (to remove the
LiH), and the corresponding tetra-substituted silane is separated from the ether
solution and recrystallized from benzene.

When triphenylsilane reacts with butyllithium, butyltriphenylsilane, (melting
point 86°C, yield 63.2%) is formed, together with a small amount (10.7%) of tetra-
phenylsilane.

Under the action of α-naphthyltriethoxyxilane on methylmagnesium chloride,
α-naphthylmethylethoxyxilane and trimethylethoxyxilane are formed. The reaction
apparently takes place according to the scheme:

\[
\text{Si(OC_2H_5)_3 + 2CH_3MgCl} \rightarrow \alpha-C_{10}H_7(\text{Si(OR)})_2 + 2\text{MgCl}_2(\text{OC_2H_5})
\]

It has likewise not been possible to obtain pure α-naphthyltriocetylasilane
α-C_{10}H_7Si(C_8H_{17})_3, since a mixture of this substance with α-naphthylidioctylsilane
α-C_{10}H_7Si(C_8H_{17})_2H was formed.

While in the case of the trialkylmethyls R_3C-, the ability of these radicals to
enter into the Grignard and Wurtz reactions decreases with increasing length of R
from methyl to butyl (at least for synthesis under ordinary conditions), the oppo-
site relation holds in the case of the trialkylsilanes R_3Si. It has recently been
possible to synthesize α-naphthyltrimethylsilane by means of an organolithium com-

\[
\alpha-C_{10}H_7Li + (\text{CH}_3)_3Si \rightarrow \alpha-C_{10}H_7Si(CH_3)_3 + \text{LiCl}
\]

A.D. Petrov and T.I. Chernysheva (Bibl. 91) prepared α-naphthyltrimethylsilane by
means of an organomagnesium compound.

\[ \text{CH}_3\text{C}_6\text{H}_5\text{Si(OC}_2\text{H}_5)\text{Cl} + \text{MgBrCH}_3 \rightarrow \text{CH}_3\text{C}_6\text{H}_5\text{Si(CH}_3)\text{Cl} + \text{MgClBr} \]

It is interesting to note that it was found that \( \alpha \)-naphthyltrimethylsilane could be obtained by substituting fluorine atoms for the ethoxy groups in \( \alpha \)-naphthyltriethoxysilane, followed by the action of \( \text{CH}_3\text{MgI} \) on the product so obtained.

\[ \text{CH}_3\text{C}_6\text{H}_5\text{Si(O}_2\text{C}_6\text{H}_5)\text{F} + 3\text{HF} \rightarrow \text{CH}_3\text{C}_6\text{H}_5\text{SiF}_3 + 3\text{C}_6\text{H}_5\text{OH} \]

\[ \text{CH}_3\text{C}_6\text{H}_5\text{SiF}_3 + 3\text{MgCH}_3 \rightarrow 3\text{MgF} + \text{CH}_3\text{C}_6\text{H}_5\text{Si(OC}_2\text{H}_5)\text{Cl} \]

\( \alpha \)-naphthyltriphenylsilane has also been prepared, but attempts to synthesize tetra-\( \alpha \)-naphthylsilane proved vain. Even when lithium was used instead of magnesium, and at high temperatures, only tri-\( \alpha \)-naphthylsilane could be obtained, which was evidently formed on the treatment of the reaction products with water by the formula:

\[ (\text{C}_6\text{H}_5\text{SiLi} + \text{HOH} \rightarrow \text{LiOH} + (\text{C}_6\text{H}_5\text{Si})\text{H} \]

Tetra-\( \beta \)-naphthylsilane is obtained in good yield from \( \beta \)-bromonaphthalene (Bibl.92).

It was not possible to prepare \( \alpha \)-naphthyliditolylisoamylysilane \( \text{C}_10\text{H}_7\text{Si}(\text{C}_6\text{H}_4\text{CH}_3)_2 \)

\[ \text{CH}_3 \]

\[ \text{Si-C-CH}_2\text{-CH}_3 \]

by the aid of organomagnesium compounds.

\( \alpha \)-naphthylidip-\( \beta \)-tolylethylsilane and \( \alpha \)-naphthylidip-\( \beta \)-tolylbutylsilane are prepared by this method with relative ease.

By the action of organomagnesium compounds on tetraethoxysilane, only two \( \alpha \)-naphthyl radicals could be introduced, giving \( (\text{C}_10\text{H}_7)_2\text{Si(OC}_2\text{H}_5)_2 \).

A.D.Petrov and T.I.Chernysheva (Bibl.93) has prepared silanes with two and
three α-naphthyl radicals by means of lithium, for example: \( (\alpha-C_{10}H_7)_2Si(C_4H_9)_2 \);
\( (\alpha-C_{10}H_7)_2Si(C_6H_5)_2 \); \( (\alpha-C_{10}H_7)_3SiOC_2H_5 \); \( (\alpha-C_{10}H_7)_3SiC_2H_5 \);
\( (\alpha-C_{10}H_7)_3SiC_3H_7 \).

Using organolithium compounds, alkylbiphenylysilanes have been obtained in high yield. It is interesting that in the series of the alkylbiphenylysilanes, as in the series of alkyl-α-naphthylsilanes, a lowering of the freezing point or melting point with increasing length of the alkyl radical from \( C_{12}H_9Si(CH_3)_3 \) to \( C_{12}H_9Si(C_4H_9)_3 \) has been noted.

The action of \( R_3SiCl \) on 9, 10-dilithium-9, 10-dihydroanthracene by formulas I and II has yielded 9, 10-dihydroanthracene-9, 10-di(trialkylsilanes). The symmetrical compounds obtained by formula II were solids (in some cases mixtures of the cis and trans isomers). The reaction by formula II usually did not proceed to completion; a mixture of mono-substituted and mixed di-substituted hydroanthracenes was obtained:

\[
\begin{align*}
\text{(I)} & \quad \text{H} \quad \text{Li} \quad + 2R_3SiCl \quad \rightarrow \quad 2\text{LiCl} + \quad \text{H} \quad \text{SiR}_3 \\
\text{(II)} & \quad \text{R}_3\text{SiCl} + \quad \text{H} \quad \text{Li} \quad + \quad \text{R}_3\text{SiCl} \quad \rightarrow \quad 2\text{LiCl} + \quad \text{H} \quad \text{SiR}_3
\end{align*}
\]

When these substances were heated to 300°C, no decomposition with liberation of anthracene was noted, but 20% HCl did split off anthracene from them, while under these same conditions, biphenyl was not liberated from a trialkylbiphenylysilane.

In 1950 a paper was published describing the synthesis, mainly by the aid of
lithium, of 19 organosilanes with sterically hindered radicals: orthotolyl, mesityl, and others (Bibl.94). A series of substituted aryltrimethylsilanes of the type:

\[
\begin{array}{c}
\text{(CH}_3\text{Si} \text{O})_2 \text{(X)} \\
\text{O} \\
\text{(CH}_3\text{Si} \text{O})_2 \text{X}
\end{array}
\]

was obtained, where \(X\) is the substituent in the ortho, meta, or para position, being \(\text{CH}_3\), \((\text{CH}_3)_3\text{Si}\), \(\text{C}_6\text{H}_5\) etc. In addition the physical properties and infrared spectra of these compounds were studied.

It has, finally, recently been possible to prepare (Bibl.95) tricyclohexylchlorosilane \((\text{C}_6\text{H}_{11})_3\text{SiCl}\), but only by using lithium. In this compound, however, even by the aid of the corresponding organolithium compounds, the chlorine could not be replaced by a \(\text{C}_6\text{H}_5\), \(\text{C}_2\text{H}_5\) or \(\text{CH}_3\) group.

The yield of tetratolyldisilanes on their synthesis from para, meta, and orthotolylmagnesium bromides and \(\text{SiCl}_4\), respectively, is 35%, 8% and 0%; and it was not possible to obtain o-tetratolylsilane, when sodium, or even lithium, was used instead of magnesium. In the case of lithium, used at a temperature of 170°C, two substances with melting points of 230°C and 340°C were obtained (Bibl.95) which, according to the analytical results, correspond to one and the same formula \((\text{CH}_3\text{C}_6\text{H}_4)_4\text{Si}\).

When isopropyllithium acts on \(\text{HSiCl}_3\), it has been possible to replace only three chlorine atoms by isopropyl groups; tert-butylithium, at the boiling point of pentane, is able to replace only one atom of chlorine in \(\text{SiCl}_4\) by tert-butyl. A second tertiary butyl group is introduced only at an elevated temperature (70°C), while it has not been possible to introduce a third and fourth group under any conditions.

In the reaction of alkyl-(aryl)-lithium \((\text{RZ}_2)\) with \(\text{SiCl}_4\), the radicals can be
arranged in order of decreasing reactivity in the following order:

Ye.N. Soshestvenskaya (Bibl. 96) obtained tetrabenzylsilane by the action of potassium fluosilicate on benzylmagnesium chloride:

$$4C_{6}H_{5}CH_{2}MgCl + K_{2}SiF_{6} \rightarrow (C_{6}H_{5}CH_{2})_{4}Si + 2MgCl_{2} + 2MgF_{2} \cdot 2K$$

Potassium fluosilicate reacts more readily than sodium fluosilicate.

Tetra-substituted silanes are obtained from organosilicon compounds whose molecule contains the Si-OR and Si-H groups by the action of an alloy of sodium and potassium (Bibl. 94).

By the action of indenylsodium and indenyllithium on alkylhalosilanes, methylindenylsilanes and ethylindenylsilanes were obtained by the following reaction (Bibl. 97):

$$\text{or}$$

Organolithium compounds with multiple bonds between the carbon atoms more or less close to the silicon atom, should possess a number of specific peculiarities. In order to study such compounds, Ushakov and Itenberg have synthesized triethylvinylsilane and studied its properties. It was found that this compound is not
polymerized under the conditions studied by them (Bibl.65).

Allyltrimethylsilane was synthesized by the following method:

**Preparation of allyltrimethylsilane.** To 5.8 mols of freshly prepared allylmagnesium bromide, 542 g of trimethylchlorosilane was added during the course of 4 hours. The ether was then distilled off in a rectifying column until the temperature had reached 85°C. The residue in the flask was now heated at this temperature for 24 hours, after which it was hydrolyzed with water and distilled with steam. The organic layer was separated from the aqueous layer, dried, and fractionated in a column with 15 theoretical plates, yielding 291 g of allyltrimethylsilane; boiling point 84.9°C (737 mm); specific gravity $d_4^{20} = 0.7193$. The yield was 51% of theoretical.

Diallyldiethylsilane was first prepared by B.N. Yakovlev (Bibl.98) by the action of allylmagnesium bromide on diethylchlorosilane:

$$2\text{CH}_2=\text{CH}-\text{CH}_2\text{MgBr} + (\text{C}_2\text{H}_5)_2\text{SiCl}_2 \rightarrow (\text{CH}_2=\text{CH}-\text{CH}_2)\text{Si}(\text{C}_2\text{H}_5)_2 + \text{MgCl}_2 + \text{MgBr}_2$$

The yield of diallyldiethylsilane was 60% of theoretical; boiling point 91 - 92°C (34 mm); specific gravity $d_4^{20} = 0.8076$; index of refraction $n_D^{25} = 1.4594$.

The product is polymerized under the action of peroxides.

The synthesis of substituted silanes with unsaturated organic radicals has recently attracted great attention. A.D. Petrov and associates (Bibl.99) have synthesized a large number of unsaturated organosilanes by the action of organomagnesium and organolithium compounds on halosilanes, chloroalkyltrialkyl-(aryl)-silanes and alkyl-(aryl)-halosilanes. They obtained compounds containing double bonds, double and triple bonds, etc., in the organic radical by the reactions:

$$((\text{C}_2\text{H}_5)_2\text{Si})_2\text{CHBr} + \text{BrMgCl}_2\text{CH}=\text{CH}_2 \rightarrow$$

$$\text{Cl}_3\text{H}_7$$

$$\rightarrow (\text{C}_2\text{H}_5)_2\text{Si}-\text{CH}_2-\text{CH}-(\text{C}_2\text{H}_5) + \text{MgBr}_2$$

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Triphenylvinylsilane was prepared by the action of phenyllithium on vinyltrichlorosilane:

\[ (\text{CH}_3)_3SiCl + \text{BrMgBr} \rightarrow \text{C} = \text{C} + \text{CH}_2 \rightarrow (\text{CH}_3)_3\text{SiC} = \text{C} = \text{CH}_2 + \text{MgBr} \]

Substituted silanes containing the vinyl radical were likewise prepared by the action of a Grignard reagent on vinyltrichlorosilane (Bibl.100):

\[ \text{CH}_2 = \text{CHSiCl}_2 + 3\text{C}_6\text{H}_5\text{MgBr} \rightarrow \text{CH}_2 = \text{CHSi(C}_6\text{H}_5)_3 + 3\text{MgClBr} \]

This reaction proceeds in good yield.

**Physical Properties**

Many papers have recently appeared on the synthesis and study of the physical properties of various tetraalkylsilanes. Papers on the properties of the new tetraalkylsilanes, tetraarylsilanes, and mixed tetraalkyl-(aryl)-silanes are of great interest (Bibl.69).

Figures 4 and 5 show graphically the variation of certain physical properties of tetra-substituted silanes with the number of carbon atoms in the molecule (for comparison the variation of the same properties of the hydrocarbons is also shown) (Bibl.101).

Table 12 gives the physical properties of mixed tetra-substituted silanes.

Table 13 gives more detailed data on the physical properties of mixed trimethyl- and triethyl-tetra-substituted silanes. The boiling point and specific gravity of tetra-substituted silanes depend strongly on the size and structure of the radicals entering into their molecules, and on the symmetry of the molecule as a whole.

Table 14 gives data on the physical properties of tetra-substituted silanes.
### Table 12
Physical Properties of Mixed Tetra-Substituted Silanes

<table>
<thead>
<tr>
<th>a) Name</th>
<th>b) Formula</th>
<th>c) Melting Point, °C</th>
<th>d) Boiling Point, °C</th>
<th>e) Specific Gravity, d_20</th>
<th>f) Refractive Index, n_25</th>
<th>g) Molecular Refraction</th>
<th>h) Bibliography</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trimethylsilane</td>
<td>(CH_3)_3SiH</td>
<td>-</td>
<td>-</td>
<td>0.6849</td>
<td>1.3828 (20°)</td>
<td>-</td>
<td>23, 69, 140</td>
</tr>
<tr>
<td>Trimethylpropylsilane</td>
<td>(CH_3)_3SiC(CH_3)_2</td>
<td>-</td>
<td>70</td>
<td>0.7020</td>
<td>1.3908</td>
<td>39, 69</td>
<td>23, 69, 140</td>
</tr>
<tr>
<td>Trimethylbutylsilane</td>
<td>(CH_3)_3SiC(CH_2)_2</td>
<td>-</td>
<td>-</td>
<td>0.4039</td>
<td>1.4394 (20°)</td>
<td>42, 00</td>
<td>23, 69</td>
</tr>
<tr>
<td>Trimethyliso- butylsilane</td>
<td>(CH_3)_3SiC(CH_3)_2</td>
<td>-</td>
<td>-</td>
<td>0.7181</td>
<td>1.4091</td>
<td>42, 00</td>
<td>23, 69</td>
</tr>
<tr>
<td>Trimethyl-tert-butylsilane</td>
<td>(CH_3)_3SiC(CH_3)_2</td>
<td>76</td>
<td>103</td>
<td>0.7322</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Trimethylmethyisilane</td>
<td>(CH_3)_3SiC(CH_3)_2</td>
<td>-</td>
<td>139</td>
<td>0.7513</td>
<td>1.4096</td>
<td>-</td>
<td>23, 69</td>
</tr>
<tr>
<td>Trimethylisopropylsilane</td>
<td>(CH_3)_3SiC(CH_3)_2</td>
<td>-</td>
<td>131.5</td>
<td>0.7320</td>
<td>1.4057</td>
<td>48, 92</td>
<td>23, 140</td>
</tr>
<tr>
<td>Trimethylhexylsilane</td>
<td>(CH_3)_3SiC(CH_2)_2</td>
<td>-</td>
<td>163</td>
<td>0.7422</td>
<td>1.4154</td>
<td>-</td>
<td>69</td>
</tr>
<tr>
<td>Trimethylheptylsilane</td>
<td>(CH_3)_3SiC(CH_2)_2</td>
<td>-</td>
<td>184</td>
<td>0.7566</td>
<td>1.4201</td>
<td>-</td>
<td>69</td>
</tr>
<tr>
<td>Trimethyloctylsilane</td>
<td>(CH_3)_3SiC(CH_2)_2</td>
<td>-</td>
<td>202</td>
<td>0.7911</td>
<td>1.4242</td>
<td>-</td>
<td>69</td>
</tr>
<tr>
<td>Trime thyldecylsilane</td>
<td>(CH_3)_3SiC(CH_2)_2</td>
<td>-</td>
<td>240</td>
<td>0.7900</td>
<td>1.4310</td>
<td>-</td>
<td>69</td>
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<tr>
<td>Trimethylundecylsilane</td>
<td>(CH_3)_3SiC(CH_2)_2</td>
<td>-</td>
<td>273</td>
<td>0.7900</td>
<td>1.4358</td>
<td>-</td>
<td>69</td>
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<tr>
<td>Trimethylundecylsilane</td>
<td>(CH_3)_3SiC(CH_2)_2</td>
<td>-</td>
<td>273</td>
<td>0.7900</td>
<td>1.4358</td>
<td>-</td>
<td>69</td>
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<tr>
<td>Trimethyltetradecylsilane</td>
<td>(CH_3)_3SiC(CH_2)_2</td>
<td>-</td>
<td>300</td>
<td>0.7511</td>
<td>1.4410</td>
<td>-</td>
<td>69</td>
</tr>
<tr>
<td>Trimethylpentadecylsilane</td>
<td>(CH_3)_3SiC(CH_2)_2</td>
<td>-</td>
<td>300</td>
<td>0.7511</td>
<td>1.4410</td>
<td>-</td>
<td>69</td>
</tr>
<tr>
<td>Trimethylhexadecylsilane</td>
<td>(CH_3)_3SiC(CH_2)_2</td>
<td>171.6</td>
<td>0.873</td>
<td>-</td>
<td>-</td>
<td>133, 140, 158</td>
<td></td>
</tr>
<tr>
<td>Trimethylheptadecylsilane</td>
<td>(CH_3)_3SiC(CH_2)_2</td>
<td>-</td>
<td>191.3</td>
<td>0.872</td>
<td>-</td>
<td>-</td>
<td>133, 140, 158</td>
</tr>
<tr>
<td>Trimethyloctadecylsilane</td>
<td>(CH_3)_3SiC(CH_2)_2</td>
<td>95.8</td>
<td>0.7214</td>
<td>-</td>
<td>-</td>
<td>133, 140, 158</td>
<td></td>
</tr>
<tr>
<td>Trimethylundecylsilane</td>
<td>(CH_3)_3SiC(CH_2)_2</td>
<td>-</td>
<td>141.5</td>
<td>0.7414</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Trimethylundecylsilane</td>
<td>(CH_3)_3SiC(CH_2)_2</td>
<td>-</td>
<td>141.5</td>
<td>0.7555</td>
<td>1.4113</td>
<td>-</td>
<td>23, 140</td>
</tr>
<tr>
<td>Dimethylphenylsilane</td>
<td>(C_6H_5)_2SiH</td>
<td>176 (45 μm)</td>
<td>176 (45 μm)</td>
<td>7.343</td>
<td>-</td>
<td>-</td>
<td>147</td>
</tr>
<tr>
<td>Dimethylphenylsilane</td>
<td>(C_6H_5)_2SiH</td>
<td>-</td>
<td>120.4</td>
<td>0.7259</td>
<td>1.4062</td>
<td>44, 10</td>
<td>159</td>
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<tr>
<td>Dimethylphenylsilane</td>
<td>(C_6H_5)_2SiH</td>
<td>-</td>
<td>138</td>
<td>0.7463</td>
<td>-</td>
<td>-</td>
<td>23, 140</td>
</tr>
<tr>
<td>Dimethylphenylsilane</td>
<td>(C_6H_5)_2SiH</td>
<td>-</td>
<td>191</td>
<td>0.801</td>
<td>1.4130</td>
<td>-</td>
<td>133, 140, 158</td>
</tr>
<tr>
<td>Dimethylphenylsilane</td>
<td>(C_6H_5)_2SiH</td>
<td>-</td>
<td>277</td>
<td>0.801</td>
<td>1.4160</td>
<td>-</td>
<td>69, 142</td>
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</tbody>
</table>

a) Name; b) Formula; c) Melting Point, °C; d) Boiling Point, °C; e) Specific Gravity, d_20; f) Refractive Index, n_25; g) Molecular Refraction; h) Bibliography
Table 12, Continued

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<thead>
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<th>a)</th>
<th>b)</th>
<th>c) °C</th>
<th>d) °C</th>
<th>e) d&lt;sub&gt;4&lt;/sub&gt;</th>
<th>f) n&lt;sub&gt;D&lt;/sub&gt;</th>
<th>g)</th>
<th>h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyltriphenylsilane</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;Si(C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>67</td>
<td>173</td>
<td>0.7724</td>
<td>1.4308</td>
<td>—</td>
<td>143,144,145</td>
</tr>
<tr>
<td>Triethylpropylsilane</td>
<td>(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;SiCH&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>—</td>
<td>—</td>
<td>0.7683</td>
<td>1.42866</td>
<td>53.11</td>
<td>69,133,140</td>
</tr>
<tr>
<td>Triethylbutylsilane</td>
<td>(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;SiCH&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>192</td>
<td>1.7742</td>
<td>1.4358</td>
<td>57.77</td>
<td>—</td>
<td>159</td>
</tr>
<tr>
<td>Triethyloxobutylsilane</td>
<td>(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;SiCH&lt;sub&gt;2&lt;/sub&gt;(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>—</td>
<td>187</td>
<td>0.784</td>
<td>1.43223</td>
<td>—</td>
<td>159</td>
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<td>Triethyltrimethylsilane</td>
<td>(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;SiCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>—</td>
<td>211</td>
<td>0.7758</td>
<td>1.4333</td>
<td>57.78</td>
<td>159</td>
</tr>
<tr>
<td>Triethylhexylsilane</td>
<td>(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;SiCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>—</td>
<td>205</td>
<td>0.785</td>
<td>1.4377</td>
<td>—</td>
<td>69</td>
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<td>Triethyloctylsilane</td>
<td>(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;SiCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>230</td>
<td>0.7880</td>
<td>1.4361</td>
<td>62.45</td>
<td>65,87,88</td>
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</tr>
<tr>
<td>Triethyldecylsilane</td>
<td>(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;SiCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>—</td>
<td>247</td>
<td>0.7807</td>
<td>1.4442</td>
<td>—</td>
<td>69</td>
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<tr>
<td>Triethylhexylsilane</td>
<td>(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;SiCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>—</td>
<td>262</td>
<td>0.7917</td>
<td>1.4438</td>
<td>—</td>
<td>69</td>
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<tr>
<td>Triethylbenzylsilane</td>
<td>(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;SiCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>—</td>
<td>293</td>
<td>0.8036</td>
<td>1.4472</td>
<td>—</td>
<td>69</td>
</tr>
<tr>
<td>Triethyl-p-ethylphenylsilane</td>
<td>(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;SiCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>—</td>
<td>238</td>
<td>0.906 (U&lt;sup&gt;2&lt;/sup&gt;)</td>
<td>—</td>
<td>—</td>
<td>73,131,140</td>
</tr>
<tr>
<td>Diethylidipropylsilane</td>
<td>(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;Si(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>—</td>
<td>268</td>
<td>0.906 (U&lt;sup&gt;2&lt;/sup&gt;)</td>
<td>—</td>
<td>—</td>
<td>32</td>
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<tr>
<td>Diethylidinonylsilane</td>
<td>(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;Si(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>—</td>
<td>117</td>
<td>0.895</td>
<td>1.4400</td>
<td>—</td>
<td>107</td>
</tr>
<tr>
<td>Diethylidiphenylsilane</td>
<td>(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;Si(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>—</td>
<td>190</td>
<td>1.4422</td>
<td>—</td>
<td>—</td>
<td>52</td>
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<tr>
<td>Diethyldiphenylsilane</td>
<td>(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;Si(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>—</td>
<td>266—210</td>
<td>0.9831</td>
<td>1.4472</td>
<td>—</td>
<td>85,87,88</td>
</tr>
<tr>
<td>Diethylphenyl-(p-ethylphenyl)-silane</td>
<td>(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Si(CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>—</td>
<td>170</td>
<td>1.4438</td>
<td>—</td>
<td>—</td>
<td>29,30,71,84,88</td>
</tr>
<tr>
<td>Ethyltriphenylsilane</td>
<td>(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;Si(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>76</td>
<td>0.9831</td>
<td>1.4472</td>
<td>—</td>
<td>—</td>
<td>47,140,141</td>
</tr>
<tr>
<td>Dipropylethylbenzylsilane</td>
<td>(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;Si(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>—</td>
<td>178</td>
<td>0.9831</td>
<td>1.4472</td>
<td>—</td>
<td>47,140,141</td>
</tr>
<tr>
<td>Dibenzylethylsilane</td>
<td>(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;Si(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>—</td>
<td>265</td>
<td>0.9831</td>
<td>1.4472</td>
<td>—</td>
<td>47,140,141</td>
</tr>
<tr>
<td>Methyleneethylpropylsilane</td>
<td>(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;Si(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>—</td>
<td>220—230</td>
<td>0.9831</td>
<td>1.4472</td>
<td>—</td>
<td>47,140,141</td>
</tr>
<tr>
<td>Methyleneethylpropylsilane</td>
<td>(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;Si(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>—</td>
<td>250</td>
<td>0.9831</td>
<td>1.4472</td>
<td>—</td>
<td>47,140,141</td>
</tr>
<tr>
<td>Methyleneethylpropylsilane</td>
<td>(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;Si(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>—</td>
<td>282</td>
<td>0.9831</td>
<td>1.4472</td>
<td>—</td>
<td>47,140,141</td>
</tr>
<tr>
<td>Ethylpropylenezylsilane</td>
<td>(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;Si(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>—</td>
<td>325—200</td>
<td>0.9831</td>
<td>1.4472</td>
<td>—</td>
<td>47,140,141</td>
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</table>

a) Name; b) Formula; c) Melting Point, °C; d) Boiling Point, °C; e) Specific Gravity, d<sub>4</sub><sup>20</sup>; f) Refractive Index, n<sub>D</sub><sup>25</sup>; g) Molecular Refraction; h) Bibliography
### Table 13

Physical Properties of Mixed Trimethyl- and Triethyl-Substituted Silanes (Bibl.157)

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c) °C</th>
<th>d)</th>
<th>e)</th>
<th>f)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>(CH₃)₃Si(CH₃)₂</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Trimethylsilane</td>
<td>(CH₃)₃SiCH₃</td>
<td>25</td>
<td>7200</td>
<td>0.7040</td>
<td>0.422</td>
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<tr>
<td>Trimethylpropylsilane</td>
<td>(CH₃)₃Si(C₂H₅)</td>
<td>49</td>
<td>7500</td>
<td>0.7197</td>
<td>0.479</td>
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<tr>
<td>Trimethylbutylsilane</td>
<td>(CH₃)₃Si(C₃H₇)</td>
<td>74</td>
<td>8000</td>
<td>0.7352</td>
<td>0.658</td>
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<tr>
<td>Trimethylamylsilane</td>
<td>(CH₃)₃Si(C₄H₉)</td>
<td>95</td>
<td>9200</td>
<td>0.7477</td>
<td>0.670</td>
</tr>
<tr>
<td>Trimethylhexylsilane</td>
<td>(CH₃)₃Si(C₆H₁₃)</td>
<td>117</td>
<td>9800</td>
<td>0.7578</td>
<td>0.847</td>
</tr>
<tr>
<td>Trimethylheptylsilane</td>
<td>(CH₃)₃Si(C₇H₁₇)</td>
<td>137</td>
<td>10600</td>
<td>0.7659</td>
<td>1.105</td>
</tr>
<tr>
<td>Trimethyloctylsilane</td>
<td>(CH₃)₃Si(C₈H₁₇)</td>
<td>156</td>
<td>11700</td>
<td>0.7729</td>
<td>1.142</td>
</tr>
<tr>
<td>Trimethyldecylsilane</td>
<td>(CH₃)₃Si(C₁₀H₂₁)</td>
<td>191</td>
<td>12800</td>
<td>0.7848</td>
<td>2.261</td>
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<tr>
<td>Trimethylundecylsilane</td>
<td>(CH₃)₃Si(C₁₁H₂₃)</td>
<td>222</td>
<td>14100</td>
<td>0.7938</td>
<td>3.489</td>
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<tr>
<td>Triethylmethylsilane</td>
<td>(C₂H₅)₃SiCH₃</td>
<td>84</td>
<td>8600</td>
<td>0.7668</td>
<td>5.106</td>
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<tr>
<td>Triethylpropylsilane</td>
<td>(C₂H₅)₃Si(C₂H₅)</td>
<td>127</td>
<td>9400</td>
<td>0.7423</td>
<td>2.083</td>
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<tr>
<td>Triethylbutylsilane</td>
<td>(C₂H₅)₃Si(C₃H₇)</td>
<td>144</td>
<td>11000</td>
<td>0.7931</td>
<td>1.351</td>
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<td>Triethylamylsilane</td>
<td>(C₂H₅)₃Si(C₄H₉)</td>
<td>162</td>
<td>11500</td>
<td>0.7545</td>
<td>1.185</td>
</tr>
<tr>
<td>Triethylhexylsilane</td>
<td>(C₂H₅)₃Si(C₆H₁₃)</td>
<td>179</td>
<td>11700</td>
<td>0.8018</td>
<td>1.515</td>
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<tr>
<td>Triethylheptylsilane</td>
<td>(C₂H₅)₃Si(C₇H₁₇)</td>
<td>196</td>
<td>11900</td>
<td>0.8045</td>
<td>1.818</td>
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<tr>
<td>Triethyloctylsilane</td>
<td>(C₂H₅)₃Si(C₈H₁₇)</td>
<td>204</td>
<td>12900</td>
<td>0.8018</td>
<td>1.980</td>
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<tr>
<td>Triethyldecylsilane</td>
<td>(C₂H₅)₃Si(C₁₀H₂₁)</td>
<td>241</td>
<td>14800</td>
<td>0.8175</td>
<td>3.705</td>
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a) Name; b) Formula; c) Boiling Point, °C, at 200 mm; d) Calculated Heat of Vaporization, cal/mol; e) Specific Gravity; f) Absolute Viscosity, Centipoises
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<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c)</th>
<th>d) $\rho_{4}^{25}$</th>
<th>e) $n_{D}^{20}$</th>
<th>f)</th>
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<td>Vinyltrimethylsilane</td>
<td>CH$_2$=CHSi(CH$_3$)$_2$</td>
<td>54.4</td>
<td>0.6865</td>
<td>1.3880</td>
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<td>Vinyltriethyilsilane</td>
<td>CH$_2$=CHSi(CH$_2$)$_2$</td>
<td>144.0</td>
<td>0.7674</td>
<td>1.4340</td>
<td>65</td>
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<tr>
<td>Vinyltripropyllsilane</td>
<td>CH$_2$=CHSi(CH$_3$)$_3$</td>
<td>73.0</td>
<td>0.8310</td>
<td>1.4432</td>
<td>99</td>
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<tr>
<td>Vinyltributylsilane</td>
<td>CH$_2$=CHSi(CH$_3$)$_3$</td>
<td>99.65</td>
<td>0.8261</td>
<td>1.4479</td>
<td>100</td>
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<tr>
<td>Vinyltrimethylsilane</td>
<td>CH$_2$=CHSi(C$_6$H$_5$)$_2$</td>
<td>145.3</td>
<td>0.8078</td>
<td>1.4480</td>
<td>100</td>
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<tr>
<td>Vinyltriallylsilane</td>
<td>CH$_2$=CHSi(C$_6$H$_5$)$_3$</td>
<td>69.7</td>
<td>0.8313</td>
<td>1.4790</td>
<td>100</td>
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<td>Vinyltriphenylsilane</td>
<td>CH$_2$=CHSi(C$_6$H$_5$)$_3$</td>
<td>m.p.</td>
<td>58-59</td>
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<td>Vinyltribenzylsilane</td>
<td>CH$_2$=CHSi(C$_6$H$_5$)$_3$</td>
<td>m.p.</td>
<td>76.7-77.5</td>
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<td>β-Dromovinyltriethyilsilane</td>
<td>CHBr=CHSi(C$_6$H$_5$)$_3$</td>
<td>66.0-67.0</td>
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<td>1.4770</td>
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<td>Styriltriphenylsilane</td>
<td>C$_6$H$_5$CH=CHSi(C$_6$H$_5$)$_3$</td>
<td>m.p.</td>
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<td>Allyltrimethylsilane</td>
<td>C$_2$H$_5$=CH=CH$_2$Si(C$_2$H$_5$)</td>
<td>84.9</td>
<td>0.7193</td>
<td>1.4074</td>
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<td>Allyltriethyilsilane</td>
<td>C$_2$H$_5$=CH=CH$_2$Si(C$_2$H$_5$)</td>
<td>170-172</td>
<td>753</td>
<td>0.7873</td>
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<td>Allyltripropyllsilane</td>
<td>C$_2$H$_5$=CH=CH$_2$Si(C$_2$H$_5$)</td>
<td>217.0</td>
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<td>99,128</td>
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<td>C$_2$H$_5$=CH=CH$_2$Si(C$_2$H$_5$)</td>
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<td>C$_2$H$_5$=CH=CH$_2$Si(C$_6$H$_5$)$_2$</td>
<td>213.6</td>
<td>0.8911</td>
<td>1.5090</td>
<td>99</td>
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<td>C$_2$H$_5$=CH=CH$_2$SiC$_2$H$_5$</td>
<td>310-311</td>
<td>740</td>
<td>0.9876</td>
<td>1.5660</td>
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<td>Allylmethylidiphenylsilane</td>
<td>C$_2$H$_5$=CH=CH$_2$-Si(C$_6$H$_5$)(C$_6$H$_5$)CH$_2$=CHH$_2$</td>
<td>283</td>
<td></td>
<td></td>
<td>99</td>
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<tr>
<td>Allylhexyloxybutylbenzyllsilane</td>
<td>(CH$_2$=CH)=$\text{CH}_2$Si(C$_6$H$_5$)$_2$</td>
<td>136.8</td>
<td>0.7679</td>
<td>1.4420</td>
<td>67</td>
</tr>
<tr>
<td>Lillyltrimethylsilane</td>
<td>(CH$_2$=CH)=$\text{CH}_2$Si(C$_2$H$_5$)$_3$</td>
<td>91-92</td>
<td>0.8076</td>
<td>1.4594</td>
<td>99</td>
</tr>
<tr>
<td>Diallyldiethyilsilane</td>
<td>(CH$_2$=CH)=$\text{CH}_2$Si(CH$_3$)$_2$</td>
<td>180.3</td>
<td>0.8065</td>
<td>1.4662</td>
<td>52,96</td>
</tr>
<tr>
<td>Triallylmethylsilane</td>
<td>(CH$_2$=CH)=$\text{CH}_2$Si(C$_6$H$_5$)$_3$</td>
<td>105-106</td>
<td>34</td>
<td>0.8237</td>
<td>1.4723</td>
</tr>
<tr>
<td>Triallylethylsilane</td>
<td>(CH$_2$=CH)=$\text{CH}_2$SiC$_2$H$_5$</td>
<td>218.3</td>
<td>0.8178</td>
<td>1.4706</td>
<td>52</td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Boiling Point, °C; d) Specific Gravity, $\rho_{4}^{25}$; e) Refractive Index, $n_{D}^{20}$; f) Bibliography
<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c)</th>
<th>d)</th>
<th>e)</th>
<th>f)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Triallylbutylsilane</strong></td>
<td>$\text{CH}_3\text{CH}=$CH$_2$Si(C$_2$H$_5$)$_2$</td>
<td>108 (11 mm)</td>
<td>0.8200</td>
<td>1.4722</td>
<td>99</td>
</tr>
<tr>
<td><strong>Triallylphenylsilane</strong></td>
<td>$\text{CH}_3\text{CH}=$CH$_2$Si(C$_6$H$_5$)$_2$</td>
<td>274.8 (751 mm)</td>
<td>0.9174</td>
<td>1.5300</td>
<td>99</td>
</tr>
<tr>
<td><strong>Triallylcyclohexylsilane</strong></td>
<td>$\text{CH}_3\text{CH}=$CH$_2$Si(C$_6$H$_11$)$_2$</td>
<td>127–129 (13 mm)</td>
<td>0.8659</td>
<td>1.4790</td>
<td>99</td>
</tr>
<tr>
<td><strong>Triallyl-d-naphthylsilane</strong></td>
<td>$\text{CH}_3\text{CH}=$CH$_2$Si(C$_7$H$_8$)$_2$</td>
<td>194–196 (10 mm)</td>
<td>0.9928</td>
<td>1.5872</td>
<td>99</td>
</tr>
<tr>
<td><strong>Tetraallylsilane</strong></td>
<td>$\text{CH}_2\text{CH}=$CH$_2$Si(CH$_3$)$_2$</td>
<td>111.5–112 (750 mm)</td>
<td>0.7358</td>
<td>1.4148</td>
<td>99</td>
</tr>
<tr>
<td><strong>Butylenetriethylsilane</strong></td>
<td>$\text{CH}_3$</td>
<td>188.5 (750 mm)</td>
<td>0.7994</td>
<td>1.4505</td>
<td>99</td>
</tr>
<tr>
<td><strong>Isobutylenetriethylsilane</strong></td>
<td>$\text{CH}_2\text{C}=$CH$_2$Si(C$_2$H$_5$)$_3$</td>
<td>178–185 (758 mm)</td>
<td>0.8012</td>
<td>1.4515</td>
<td>99</td>
</tr>
<tr>
<td><strong>Diisobutylenedimethylsilane</strong></td>
<td>$\text{CH}_3$</td>
<td>231.9 (750 mm)</td>
<td>0.8338</td>
<td>1.4772</td>
<td>99</td>
</tr>
<tr>
<td><strong>Triisobutylenemethylsilane</strong></td>
<td>$\text{CH}_3$</td>
<td>269.5 (745 mm)</td>
<td>0.8809</td>
<td>1.4950</td>
<td>99</td>
</tr>
<tr>
<td><strong>Tetraisobutylenesilane</strong></td>
<td>$\text{CH}_3$</td>
<td>74–75 (19 mm)</td>
<td>0.7988</td>
<td>1.4585</td>
<td>99</td>
</tr>
<tr>
<td><strong>Pentadienetriethylsilane</strong></td>
<td>$\text{CH}_3\text{CH}=$CH=CHSi(C$_2$H$_5$)$_2$</td>
<td>206–207 (760 mm)</td>
<td>0.7971</td>
<td>1.4460</td>
<td>99</td>
</tr>
<tr>
<td><strong>Amylenetriethylsilane</strong></td>
<td>$\text{CH}_3\text{CH}=$CH=CH$_2$Si(C$_2$H$_5$)$_2$</td>
<td>200–201 (747 mm)</td>
<td>0.8021</td>
<td>1.4500</td>
<td>99</td>
</tr>
<tr>
<td><strong>Allyl-(2-methyl-4-pentenyl)-dimethylsilane</strong></td>
<td>$\text{CH}_2\text{CH}=$CH$_2$SiCH$_2$CH=CH$_2$</td>
<td></td>
<td>0.7575</td>
<td>1.4264</td>
<td>99</td>
</tr>
<tr>
<td><strong>2-Methyl-4-pentenyltrimethylsilane</strong></td>
<td>$\text{CH}_3$</td>
<td>151.3 (750 mm)</td>
<td>0.8021</td>
<td>1.4500</td>
<td>99</td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Boiling Point, °C; d) Specific Gravity, $d_2^{25}$; e) Refractive Index, $n_2^{20}$; f) Bibliography
Table 14, Continued

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c)</th>
<th>d) $d_25$</th>
<th>e) $n_D$</th>
<th>f)</th>
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</thead>
<tbody>
<tr>
<td>2-Methyl-4-pentenyltriethylsilane</td>
<td>CH$_3$-CH=CH-CH-CH$_2$Si(C$_2$H$_5$)$_2$</td>
<td>214.5 (740 mm)</td>
<td>0.8016</td>
<td>1.4502</td>
<td>94</td>
</tr>
<tr>
<td>2-Methyl-4-pentenyltriethylsilane</td>
<td>CH$_3$-CH=CH-CH$_2$Si(C$_2$H$_5$)$_2$</td>
<td>221-222 (740 mm)</td>
<td>0.8029</td>
<td>1.4510</td>
<td>94</td>
</tr>
<tr>
<td>2-Methyl-4-pentenyltrimethylsilane</td>
<td>CH$_2$-CH$_2$Si(C$_2$H$_5$)$_2$</td>
<td>255-256 (780 mm)</td>
<td>0.8098</td>
<td>1.4545</td>
<td>94</td>
</tr>
<tr>
<td>2-Methyl-4-pentenyltripropylsilane</td>
<td>CH$_3$-CH=CH-CH$_2$SiC$_3$H$_7$</td>
<td>268-269 (745 mm)</td>
<td>0.8122</td>
<td>1.4568</td>
<td>94</td>
</tr>
<tr>
<td>2-Methyl-4-pentenyltributylsilane</td>
<td>CH$_3$-CH=CH-CH$_2$SiC$_3$H$_7$</td>
<td>242 (735 mm)</td>
<td>0.8806</td>
<td>1.4896</td>
<td>99</td>
</tr>
<tr>
<td>2-Methyl-4-pentenylidimethylphenylsilane</td>
<td>CH$_3$-CH=CH-CH(C$_2$H$_5$)$_2$</td>
<td>236.5 (740 mm)</td>
<td>0.8208</td>
<td>1.4590</td>
<td>94</td>
</tr>
<tr>
<td>2-Limethyl-4-pentenyltriethylsilane</td>
<td>CH$_3$-CH=CH-CH$_2$Si(C$_2$H$_5$)$_2$</td>
<td>231.5 (750 mm)</td>
<td>0.830</td>
<td>1.4630</td>
<td>94</td>
</tr>
<tr>
<td>Cyclopentadienytriethylsilane</td>
<td>CH=CH-CH=CH$_2$Si(C$_2$H$_5$)$_2$</td>
<td>187 (7 mm)</td>
<td>0.945</td>
<td>1.5423</td>
<td>147</td>
</tr>
<tr>
<td>Indenyltrimethylsilane</td>
<td>CH=CH-CH$_2$Si(C$_2$H$_5$)$_2$</td>
<td>121 (3 mm)</td>
<td>0.950</td>
<td>1.5420</td>
<td>147</td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Boiling Point, °C; d) Specific Gravity, $d_25$; e) Refractive Index, $n_D$; f) Bibliography
<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c) ( ^\circ \text{C} )</th>
<th>d) ( d_4^{25} )</th>
<th>e) ( n_D^{20} )</th>
<th>f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indenyldi-(trimethylsilane)</td>
<td>[ \text{CH} = \text{CH} \text{Si(CH}_3\text{)}_2 ]</td>
<td>106 (3 mm)</td>
<td>0.930</td>
<td>1.3307</td>
<td>147</td>
</tr>
<tr>
<td>Indenyldi-(triethylsilane)</td>
<td>[ \text{CH} = \text{CH} \text{Si(} \text{CH}_3\text{)}_3 ]</td>
<td>190 (6 mm)</td>
<td>0.940</td>
<td>1.5335</td>
<td>147</td>
</tr>
<tr>
<td>Diindenyl(dimethy)silane</td>
<td>[ \text{CH}_2 \begin{array}{c} \text{Si(} \text{CH}_3\text{)}_2 \end{array} ]</td>
<td>155 (4 mm)</td>
<td>1.060</td>
<td>1.6110</td>
<td>147</td>
</tr>
<tr>
<td>Phenylacetylenyltriphenylsilane</td>
<td>[ (\text{C}_6\text{H}_5)_2\text{SiC}≡\text{C}–\text{C}_6\text{H}_5 ]</td>
<td>m.p. 96–98</td>
<td></td>
<td></td>
<td>160</td>
</tr>
<tr>
<td>3,4-Eth-(methyl)-vinylacetylenyltriphenylsilane</td>
<td>[ (\text{C}_6\text{H}_5)_2\text{SiC}≡\text{C}–\text{C}_6\text{H}_5 ]</td>
<td>155–156 (20 mm)</td>
<td></td>
<td></td>
<td>160</td>
</tr>
<tr>
<td>Vinylacetylenyltrimethylsilane</td>
<td>[ (\text{CH}_2)_3\text{SiC}≡\text{C}–\text{CH=CH}_2 ]</td>
<td>52–53 (80 mm)</td>
<td>0.7714</td>
<td>1.4510</td>
<td>99</td>
</tr>
<tr>
<td>Vinylacetylenyltripropylsilane</td>
<td>[ (\text{C}_3\text{H}_7)_3\text{SiC}≡\text{C}–\text{CH=CH}_2 ]</td>
<td>87–89 (7 mm)</td>
<td>0.8173</td>
<td>1.4700</td>
<td>99</td>
</tr>
<tr>
<td>Vinylacetylenyltributylsilane</td>
<td>[ (\text{C}_4\text{H}_9)_3\text{SiC}≡\text{C}–\text{CH=CH}_2 ]</td>
<td>108–110 (8 mm)</td>
<td>0.8201</td>
<td>1.4700</td>
<td>99</td>
</tr>
<tr>
<td>Li-(vinylacetylenyl)dipropylsilane</td>
<td>[ (\text{CH}_2)_2\text{SiC}≡\text{C}–\text{CH=CH}_2 ]</td>
<td>67–68 (9 mm)</td>
<td>0.8495</td>
<td>1.5108</td>
<td>99</td>
</tr>
<tr>
<td>Di-(vinylacetylenyl)dipropylsilane</td>
<td>[ (\text{C}_3\text{H}_7)_2\text{SiC}≡\text{C}–\text{CH=CH}_2 ]</td>
<td>84–86 (5 mm)</td>
<td>0.8561</td>
<td>1.5145</td>
<td>99</td>
</tr>
<tr>
<td>Li-(vinylacetylenyl)diethyilsilane</td>
<td>[ (\text{CH}_2)_2\text{SiC}≡\text{C}–\text{CH=CH}_2 ]</td>
<td>84–86 (8 mm)</td>
<td>0.8565</td>
<td>1.5140</td>
<td>160</td>
</tr>
<tr>
<td>Hexamethylenacetylenylbisilane</td>
<td>[ (\text{CH}_3)_2\text{SiC}≡\text{Si(} \text{CH}_3\text{)}_2 ]</td>
<td>134–136 (757 mm)</td>
<td>0.7703</td>
<td>1.4260</td>
<td>160</td>
</tr>
<tr>
<td>Hexaethylacetylenylbisilane</td>
<td>[ (\text{C}_2\text{H}_5)_2\text{SiC}≡\text{Si(} \text{C}_2\text{H}_5\text{)}_2 ]</td>
<td>244–245 (761 mm)</td>
<td>0.8174</td>
<td>1.1568</td>
<td>160</td>
</tr>
<tr>
<td>Hexabutylacetylenylbisilane</td>
<td>[ (\text{C}_4\text{H}_9)_2\text{SiC}≡\text{Si(} \text{C}_4\text{H}_9\text{)}_2 ]</td>
<td>215–218 (23 mm)</td>
<td>0.8330</td>
<td>1.4568</td>
<td>160</td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Boiling Point, \(^\circ \text{C}\); d) Specific Gravity, \(d_4^{25}\); e) Refractive Index, \(n_D^{20}\); f) Bibliography
Table 15

Physical Properties of Mixed Tetra-Substituted Silanes Containing the α-Naphthyl Radical

<table>
<thead>
<tr>
<th>a) Name</th>
<th>b) Formula</th>
<th>c) Melting Point, °C</th>
<th>d) Boiling Point, °C</th>
<th>e) Specific Gravity, d₂₀</th>
<th>f) Bibliography</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Naphthyltrimethylsilane</td>
<td>C₁₆H₁₇Si(CH₃)₃</td>
<td>-21.5</td>
<td>118-119</td>
<td>0.9871</td>
<td>83</td>
</tr>
<tr>
<td>α-Naphthyltrimethylsilane</td>
<td>C₁₆H₁₇Si(C₂H₅)₃</td>
<td>40</td>
<td>173</td>
<td>0.9827</td>
<td>83</td>
</tr>
<tr>
<td>α-Naphthyltrimethylsilane</td>
<td>C₁₆H₁₇Si(C₆H₁₃)₃</td>
<td>-50</td>
<td>349-350</td>
<td>0.9493</td>
<td>83</td>
</tr>
<tr>
<td>α-Naphthyltrimethylsilane</td>
<td>C₁₆H₁₇Si(C₅H₆)₃</td>
<td>183-185</td>
<td>-</td>
<td>-</td>
<td>158</td>
</tr>
<tr>
<td>α-Naphthyltrimethylsilane</td>
<td>C₁₆H₁₇Si(C₅H₆)₃</td>
<td>174-176</td>
<td>-</td>
<td>-</td>
<td>83</td>
</tr>
<tr>
<td>α-Naphthyltrimethylsilane</td>
<td>C₁₆H₁₇Si(C₅H₆)₃</td>
<td>54</td>
<td>386-389</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>α-Naphthyltrimethylsilane</td>
<td>C₁₆H₁₇Si(C₅H₆)₃</td>
<td>54</td>
<td>386-389</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>α-Naphthyltrimethylsilane</td>
<td>C₁₆H₁₇Si(C₅H₆)₃</td>
<td>198-199</td>
<td>-</td>
<td>-</td>
<td>158</td>
</tr>
<tr>
<td>α-Naphthyltrimethylsilane</td>
<td>C₁₆H₁₇Si(C₅H₆)₃</td>
<td>171</td>
<td>-</td>
<td>-</td>
<td>136</td>
</tr>
<tr>
<td>α-Naphthyltrimethylsilane</td>
<td>C₁₆H₁₇Si(C₅H₆)₃</td>
<td>45</td>
<td>400-405</td>
<td>1.0184</td>
<td>158</td>
</tr>
<tr>
<td>α-Naphthyltrimethylsilane</td>
<td>C₁₆H₁₇Si(C₅H₆)₃</td>
<td>160-161</td>
<td>-</td>
<td>-</td>
<td>158</td>
</tr>
<tr>
<td>α-Naphthyltrimethylsilane</td>
<td>C₁₆H₁₇Si(C₅H₆)₃</td>
<td>45</td>
<td>224-226</td>
<td>1.0798</td>
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<tr>
<td>α-Naphthyltrimethylsilane</td>
<td>C₁₆H₁₇Si(C₅H₆)₃</td>
<td>50</td>
<td>227-229</td>
<td>1.0697</td>
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<tr>
<td>α-Naphthyltrimethylsilane</td>
<td>C₁₆H₁₇Si(C₅H₆)₃</td>
<td>208-210</td>
<td>(1.5 mm)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>α-Naphthyltrimethylsilane</td>
<td>C₁₆H₁₇Si(C₅H₆)₃</td>
<td>27</td>
<td>(1.5 mm)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>α-Naphthyltrimethylsilane</td>
<td>C₁₆H₁₇Si(C₅H₆)₃</td>
<td>40-45</td>
<td>(glass)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>α-Naphthyltrimethylsilane</td>
<td>C₁₆H₁₇Si(C₅H₆)₃</td>
<td>40-45</td>
<td>(glass)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>α-Naphthyltrimethylsilane</td>
<td>C₁₆H₁₇Si(C₅H₆)₃</td>
<td>306-310</td>
<td>(3C mm)</td>
<td>1.126</td>
<td>83</td>
</tr>
<tr>
<td>α-Naphthyltrimethylsilane</td>
<td>C₁₆H₁₇Si(C₅H₆)₃</td>
<td>256-260</td>
<td>(20 mm)</td>
<td>1.0258</td>
<td>83</td>
</tr>
<tr>
<td>α-Naphthyltrimethylsilane</td>
<td>C₁₆H₁₇Si(C₅H₆)₃</td>
<td>8</td>
<td>193-195</td>
<td>1.0119</td>
<td>136</td>
</tr>
<tr>
<td>α-Naphthyltrimethylsilane</td>
<td>C₁₆H₁₇Si(C₅H₆)₃</td>
<td>126</td>
<td>-</td>
<td>-</td>
<td>136</td>
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</table>

a) Name; b) Formula; c) Melting Point, °C; d) Boiling Point, °C; e) Specific Gravity, d₂₀; f) Bibliography

containing unsaturated radicals, while Table 15 gives data on the physical properties of tetra-substituted silanes containing α-naphthyl radicals.
Chemical Properties

A characteristic feature of the mixed tetra-substituted silanes is their tendency to rearrangement and formation of symmetrical compounds.

When triethylphenylsilane is heated, rearrangement takes place and diethylbiphenylsilane and tetraethylsilane are formed.

When triethylphenylsilane is heated under pressure in a hydrogen atmosphere, condensation takes place, as noted by Dolgov (Bibl.72), which is accompanied by the formation of symmetrical compounds and cleavage of the phenyl groups:

\[ 2(c_2H_5)_3SiH_5 \rightarrow (c_2H_5)_2Si-(c_2H_5)Si(c_2H_5)_2 + 2c_6H_{12} \]
Studying the rearrangement of many asymmetrical tetra-substituted silanes, Dolgov later reached the conclusion that the rearrangement, according to the conditions, proceeds according to either eq.(1) or eq.(2):

\[
2RSiR' \rightarrow R_2SiR' + SiR' \\
2RSiR' + H_2 \rightarrow 2RH + H_2Si-SiR'_2
\]

The former reaction takes place on simple heating of the substance, while the second occurs when it is heated in a hydrogen medium. When three like radicals and one unlike radical are attached to a silicon atom then rearrangement or destruction takes place when heated in an atmosphere of hydrogen. In this case, if the compound contains one phenyl group, it is displaced rather easily, but two phenyl groups at one silicon atom stabilize the compound, and no displacement of a phenyl group is observed in this case.

On the action of sulfuric acid on methylethylpropylphenylsilane, hydroxysilanes and benzenesulfonic acid is formed:

\[
\text{C}_4\text{H}_7\text{Si}-\text{CH}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{C}_4\text{H}_7\text{Si}-\text{CH}_3 + \text{C}_6\text{H}_5\text{SO}_3\text{H}
\]

This reaction may be used to prepare hydroxysilanes that are hard to synthesize.

The action of sulfuric acid on methylethylpropylbenzylsilane leads to cleavage of the methyl group and formation of a silanesulfonic acid through an intermediate compound, ethylpropylbenzylhydroxysilane (Bibl.102):

\[
\text{(CH}_3\text{)(C}_6\text{H}_5\text{Si)(C}_4\text{H}_7\text{)(CH}_2\text{C}_6\text{H}_5) + \text{H}_2\text{SO}_4 \rightarrow \text{C}_6\text{H}_5\text{Si}-\text{C}_3\text{H}_7 + \text{C}_6\text{H}_5\text{SO}_3\text{H}
\]
Other sulfonic acids of organosilicon compounds were synthesized later by the action of chlorosulfonic acids:

\[
(C_6H_5)(C_2H_5)(i-C_4H_9)(C_3H_7)Si + CH_2=CHCH_2OH + ClSO_2OH \rightarrow HCl + (C_3H_7)SiCH_2=CHCH_2OH
\]

Under the action of chlorosulfonic acid on \((C_6H_5)CH_2(C_2H_5)(i-C_4H_9)(C_3H_7)Si\), the cleavage of the isobutyl group occurs.

Under the action of fuming HCl on triethylphenylsilane, triethylchlorosilane is formed:

\[
(C_2H_5)_3Si(C_6H_5) + HCl \rightarrow (C_2H_5)_2SiCl + C_6H_6
\]

Under the action of an alloy of potassium and sodium, or of potassium amide, on tetra-substituted silane, trialkyl-(aryl)-potassium is formed. Phenylisopropyltriphenylsilane, for instance, undergoes the following transformation under the action of a sodium-potassium alloy in ethyl ether (Bibl.104):

\[
\begin{align*}
\text{Cl}_3 & \quad \text{Cl}_3 \\
\text{C} & \quad \text{C} \\
\text{Si} & \quad \text{Si} \\
\text{(C}_2\text{H}_5\text{)} & \quad \text{(C}_2\text{H}_5\text{)} \\
\text{H}_3 & \quad \text{H}_3
\end{align*}
\]

Trimethylbenzylsilane is converted by the action of potassium amide into trimethylsilanepotassium amide:

\[
(CH_3)_3SiCH_2=CHCH_2OH + KNH_2 \rightarrow (CH_3)_2SiNHK + CH_3C_4H_6
\]

Mixed tetra-substituted silanes with four unlike substituents possess optical activity owing to their asymmetry (Bibl.105).

The reaction between allyltrimethylsilane and various chemical compounds proceeds in two directions:
1. HBr, HI, Cl, and H₂ add on the double bond.

The addition proceeds in accordance with the Markovnikov rule. As a result of reaction with hydrogen halides, β-bromopropyltrimethylsilane and β-iodopropylytrimethylsilane are formed. When these compounds react with aqueous alkali, propylene is evolved and hydroxytrimethylsilane is formed. Under the action of a hydrogen halide on allyltrimethylsilane at high temperature, a trimethylhalosilane and propylene are formed. As a result of addition of chlorine to the double bond of allyltrimethylsilane, β, γ-dichloropropyltrimethylsilane is formed, which, by thermal decomposition, yields trimethylchlorosilane and β-chloropropylene.

2. Under the action of sulfuric acid, HCl, or bromine, on allyltrimethylsilane, cleavage of the allyl group takes place. As a result of the reaction, trimethylsilane sulfate and propylene, trimethylchlorosilane and propylene, or trimethylbromosilane and β-bromopropylene, are respectively obtained.

\[
\begin{align*}
2(\text{CH}_3)_2\text{SiCH}_2\text{Cl} = & \text{Cl} = \text{CH}_2 + \text{H}_2\text{SO}_4 \rightarrow [(\text{CH}_3)_2\text{Si}]_2\text{SO}_4 + 2\text{CH}_3\text{CH} = \text{CH}_2 \\
(\text{CH}_3)_2\text{SiCl} = & \text{Cl} = \text{CH}_2 + \text{HCl} \rightarrow (\text{CH}_3)_2\text{SiCl} + \text{CH}_2CH = \text{CH}_2 \\
(\text{CH}_3)_2\text{Si} = & \text{Cl} = \text{Cl} = \text{Cl}_4 + \text{Br}_2 \rightarrow (\text{CH}_3)_2\text{SiBr} + \text{CH}_3\text{Br} = \text{Cl} = \text{CH}_2
\end{align*}
\]

When a solution of KOH in methanol reacts with trimethylallylsilane, trimethylmethoxysilane and propylene are formed. Under the action of aluminum chloride, allyltrimethylsilane polymerizes.

**Reaction of allyltrimethylsilane with hydrogen bromide.** In a test tube with a gas inlet tube, 22.8 g of allyltrimethylsilane is placed, and 0.2 mol of dry HBr are passed in. The reaction proceeds at room temperature, but it can also proceed even at as low a temperature as -60°C. The passage of HBr is terminated when the weight gain of the test tube corresponds to the theoretical (on the basis of the addition of 1 mol of HBr to 1 mol of allyltrimethylsilane). On fractionation in a vacuum, 27.5 g of β-bromopropyltrimethylsilane is obtained, boiling point 31°C (6 mm). The yield is 70% of theoretical.
The use of benzoyl peroxide in the process of addition of HBr to allytrimethylsilane does not lead to formation of Y-bromopropyltrimethylsilane, but only \( \beta \)-bromopropyltrimethylsilane is obtained.

**Behavior of \( \beta \)-bromopropyltrimethylsilane on heating.** In a flask with reflex condenser, 13 g of \( \beta \)-bromopropyltrimethylsilane is heated at about 40°C (at a temperature over 40°C, decomposition of the substance is observed). The yield of propylene amounts to 73% of theoretical. From the residue in the flask, after fractionation, 2.9 g of trimethylbromosilane was separated; boiling point 76 - 79°C. The yield was 88% of theoretical.

**Reaction of allyltrimethylsilane and hydrogen iodide.** In a 100 ml two-necked flask, 22.8 g of allyltrimethylsilane is placed and dry hydrogen iodide is passed in. After addition of 85% of the theoretical quantity of HI by weight, the passage of HI is stopped, and the mixture is fractionated under reduced pressure, yielding 22.7 g of \( \beta \)-iodopropyltrimethylsilane; boiling point 57°C (6 mm). The yield is 48% of theoretical.

This compound fumes in the air and decomposes when heated to a temperature of about 75°C, or on reaction with dilute aqueous alkali or with anhydrous aluminum chloride. When 81 g of this product is heated for 30 minutes at 80°C, propylene is formed in 55% yield. As a result of fractionation of the residue, 31.6 g of trimethyliodosilane, boiling point 106°C, in yield 46% of theoretical, is obtained.

**Reaction of allylmethylsilane with hydrogen chloride on heating.** In a flask with reflex condenser, 22.8 g of allylmethylsilane is heated at the boiling point with at the same time HCl is passed into it for 24 hours. As a result 4.4 g of trimethylchlorosilane, boiling point 57°C, is obtained. During the reaction 15% of propylene is given off. The residue contains 10.9 g of unreacted allyltrimethylsilane.

**Reaction of allylmethylsilane with chlorine.** Into 11.4 g of allyltrimethylsilane at a temperature of -70°C, 7 g of chlorine is passed at the rate of
0.003 mol/minute. Fractionation of the reaction product under reduced pressure yielded 10.3 g (56%) of β, γ-dichloropropyltrimethylsilane, boiling 36°C (4 mm). Of this β, γ-dichloropropyltrimethylsilane, 7.2 g is heated to 90°C for 30 minutes, effecting decomposition. Fractionation of the decomposition products yielded 2.6 g of alkyl chloride with a boiling point of 44.5°C, in yield of 87% of theoretical, and 3.4 g of trimethylchlorosilane, boiling point 57°C, in yield 81% of theoretical.

Hydrogenation of allyltrimethylsilane. In the presence of a nickel catalyst, 22.8 g of allyltrimethylsilane was hydrogenated under a pressure of 1 - 3 atmospheres. After 12 hours of hydrogenation, 14.6 g of butyltrimethylsilane, boiling point 89°C, yield 63% of theoretical, was obtained.

Reaction of allyltrimethylsilane with sulfuric acid. On the reaction of allyltrimethylsilane (5.7 g) with strong sulfuric acid (2.5 g) at -20°C, 5.2 g of impure trimethylsilane sulfate was obtained, melting point 49 - 52°C. In this reaction propylene in yield of 48% of the theoretical was also formed.

Reaction of allyltrimethylsilane with bromine. In a 100 ml two-necked flask, provided with a stirrer, 22.8 g of allyltrimethylsilane and 50 ml of anhydrous ethyl ether were placed. The flask was placed in a bath with solid carbon dioxide, and 32 g of bromine were added to the mixture under vigorous stirring. Fractionation of the reaction product yielded β-bromopropylene and trimethylbromosilane. For the better separation of the products, the mixture was treated with water to convert the trimethylbromosilane into hexaethyldisiloxane. Treatment with water and fractionation of the mixture yielded 3.8 g of allyl bromide (10%), 9.4 g of hexamethyl-disiloxane (58%), and 5.2 g of 1, 2, 3-tribromopropane (7%) with a boiling point of 218°C; no β, γ-dibromopropyltrimethylsilane was obtained.

Reaction of allyltrimethylsilane with methanol. A mixture of 22.5 g of KOH, 25 ml of anhydrous methanol, and 22.8 g of allyltrimethylsilane was boiled for 24 hours in a flask with a reflex condenser. Propylene was gradually evolved during the reaction, and was absorbed by bromine. By the end of the boiling, the yield of
propylene amounted to 70% of theoretical. Fractionation of the mixture yielded 8.6 g of an azeotropic mixture of methanol and trimethylmethoxysilane (18% of the methanol by weight) with a boiling point of 50°C. The yield of trimethylmethoxysilane is about 35% of theoretical.

**Reaction of allyltrimethylsilane with sodium hydroxide.** A mixture of 20 ml of 12 N NaOH and 3 g of allylmethylsilane was boiled in a flask with reflex condenser for four days. 5% of the theoretical amount of propylene was evolved.

**Reaction of allyltrimethylsilane with aluminum chloride.** In 10 minutes, 22.8 g of allyltrimethylsilane was mixed with 2 g of anhydrous aluminum chloride, forming a viscous mixture, which was then extracted with 75 mm of pentane and washed with dilute HCl. The pentane was distilled off under reduced pressure. Fractionation of the residue yielded 12.9 g of a transparent oily polymer of boiling point 290 - 340°C (15 mm). Analysis of this product showed a silicon content higher than theoretical. This allows us to assert that in addition to simple polymerization, processes of condensation also take place here, which are connected with the cleavage of the alkyl group, so that the silicon content of the product is increased.

**TETRA-SUBSTITUTED SILANES WITH FUNCTIONAL GROUPS IN THE ORGANIC RADICAL**

The synthesis of alkyl- and aryl-substituted silanes into whose organic radicals functional groups have been introduced, has become widespread in recent times. Such functional groups include the halogens, hydroxyl groups, carboxyl groups, nitro groups, amino groups, etc. Tetra-substituted silanes containing functional groups in the organic radical are polar and susceptible of further transformation. These compounds are also interesting for the elucidation of the influence of the silicon atom on their properties, chemical activity, resistance to hydrolysis, mobility of the substituents, etc.
Tetra-Substituted Silanes with a Halogen in the Organic Radical

Methods of Preparation

As already stated, under the action of a halogen on mixed tetra-substituted silanes, substituted silanes with a halogen in the organic radical may be formed (cf. page 163). On the halogenation of arylsilanes, the halogen enters in the para position with respect to silicon. In the alkylsilanes, the halogen may enter the α, β, or γ-position with respect to the silicon atom.

In alkylphenylsilanes of the type \( R_3SiC_6H_5 \), one hydrogen atom in the phenyl may easily be replaced by a halogen atom:

\[
R_3SiC_6H_5 + Cl_2 \rightarrow R_3SiC_6H_4Cl + HCl
\]

Tetra-substituted silanes containing a halogen in the organic radical may be prepared by the action of the corresponding organomagnesium compounds; thus, for example, triethyl-p-bromophenylsilane has been prepared from p-dibromobenzene by the Grignard reaction (Bibl.106).

\[
BrC_6H_4MgBr + SiCl_4 \rightarrow BrC_6H_4SiCl_3 + MgCl_2
\]

By the same method, triethyl-p-chlorophenylsilane (Bibl.107) has been prepared from p-chlorobromobenzene (Bibl.107).

Triethyl-p-iodophenylsilane is obtained on treatment of the corresponding organomagnesium compound with iodine.

\[
(C_2H_5)_3SiC_6H_4MgBr + I_2 \rightarrow (C_2H_5)_3SiC_6H_4I + MgBr_I
\]

Trimethylchloromethylsilane is obtained in good yield on the photochemical chlorination of tetramethylsilane (Bibl.108, 85).

\[
(CH_3)_3Si + Cl_2 \rightarrow (CH_3)_3SiCH_2Cl + HCl
\]
The chlorination is accomplished in CCl₄ solution in the presence of a small quantity (2%) of P₂Cl₅.

The chlorine atom in chloromethyltrimethylsilane is more reactive than in mono-chloromethyltrimethylmethane, but less reactive than in n-hexyl chloride. This will be seen from the following data on the quantity of chlorine cleavage under the action of various saponifying agents on chloromethyltrimethylsilane (I) and on n-hexyl chloride (II):

<table>
<thead>
<tr>
<th></th>
<th>Quantity of Chlorine Cleavage, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
</tr>
<tr>
<td>CH₃COOK in absolute ethanol</td>
<td>23</td>
</tr>
<tr>
<td>CH₃COOK in glacial acetic acid</td>
<td>26</td>
</tr>
<tr>
<td>KOH in absolute ethanol</td>
<td>52</td>
</tr>
<tr>
<td>KOH in 70% ethanol</td>
<td>16</td>
</tr>
<tr>
<td>KOH, aqueous solution</td>
<td>0</td>
</tr>
</tbody>
</table>

The boiling of chloromethyltrimethylsilane with aqueous silver nitrate for 5 minutes does not lead to the formation of a precipitate of silver chloride. Under the action of sodium iodide in dry acetone on chloromethyltrimethylsilane, a halogen exchange takes place, and iodomethyltrimethylsilane is obtained, which, in contrast to all organic iodine derivatives, does not react with aqueous nor alcoholic solution of silver nitrate. When iodomethyltrimethylsilane reacts with magnesium, organomagnesium compounds are formed in good yield.

α- and β-chloroethyltrichlorosilane are obtained by the action of sulfuryl chloride on ethyltrichlorosilane in the presence of a small amount of benzoyl peroxide:

\[
2nH₅C₃H₇SiCl₃ + SOCl₂ \rightarrow (C₃H₇COO)₂·CH₃CHClSiCl₃ + CH₃C₃H₇SiCl₃
\]
Under the action of methylmagnesium bromide on the compounds so obtained, corresponding tetra-substituted compounds with a halogen in the organic radical are obtained.

\[ \text{CH}_3\text{CHClSiCl}_3 + 3\text{CH}_3\text{MgBr} \rightarrow \text{CH}_3\text{CHClSi(CH}_3)_3 + 3\text{MgClBr} \]

α-chlorobenzyltrichlorosilane, \( \text{C}_6\text{H}_5\text{CHClSiCl}_3 \), is obtained by a similar method, and by the action of a Grignard reagent can likewise be converted into a tetra-substituted silane. Attempts to use this method for the chlorination of methyltrichlorosilane and phenyltrichlorosilane were unsuccessful (Bibl.109).

The chlorination of propyltrichlorosilanes by means of sulfuryl chloride in the presence of organic peroxides yielded all three chloro-substituted products:

- α-chloropropyltrichlorosilane \( \text{CH}_3\text{CH}_2\text{CHClSiCl}_3 \) (I),
- γ-chloropropyltrichlorosilane \( \text{CH}_3\text{CHClCH}_2\text{SiCl}_3 \) (II),
- β-chloropropyltrichlorosilane \( \text{CH}_2\text{ClCH}_2\text{CH}_2\text{SiCl}_3 \) (III).

The total yield was 96% of theoretical. The ratio I : II : III was 1 : 3.5 : 3.1.

These products may be converted by the Grignard reaction into the corresponding tetra-substituted silanes with a halogen atom in the organic radical. The monochloro-derivatives of triethylchlorosilane and triethylfluorosilane were used to prepare new tetraalkylsilanes containing chlorine in the organic radical.

**Preparation of β-chloroethylmethyldiethyldisilane.** In a flask provided with a stirrer with a mercury seal, a reflux condenser, and a dropping funnel, 0.5 mol of methylmagnesium bromide in 250 ml of ethyl ether were prepared. The reagent so prepared was added over a period of 2 hours to an ether solution of 62 g of β-chloroethylmethyldiethyldichlorosilane, and then the reaction mixture was heated in a flask with a reflux condenser for 2 hours on a steam bath. The reaction product is treated with a mixture of ice and acid after which the ether layer is removed. The ether extract is washed and distilled.
β-Chloroethyldiethylphenylsilane is prepared by an analogous method.

The following are the properties of the products so obtained:

<table>
<thead>
<tr>
<th></th>
<th>β-Chloroethyldiethylmethylsilane</th>
<th>β-Chloroethyldiethylphenylsilane</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Boiling Point, °C</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 200 mm</td>
<td>125</td>
<td>219</td>
</tr>
<tr>
<td>at 760 mm</td>
<td>172</td>
<td>274</td>
</tr>
<tr>
<td><strong>Specific Gravity, d_{4}^{20}</strong></td>
<td>0.9036</td>
<td>1.0109</td>
</tr>
<tr>
<td><strong>Refractive Index, n_{D}^{20}</strong></td>
<td>1.4452</td>
<td>1.5229</td>
</tr>
<tr>
<td><strong>Molecular Refraction, MR</strong></td>
<td>48.54</td>
<td>68.51</td>
</tr>
<tr>
<td><strong>Atomic Refraction, R</strong></td>
<td>6.98</td>
<td>7.48</td>
</tr>
<tr>
<td><strong>Heat of Formation (Calculated), kcal/mol</strong></td>
<td>10,000</td>
<td>13,000</td>
</tr>
</tbody>
</table>

Trimethyl-sec-bromobutylsilane was prepared only recently by A.D. Petrov and G.I. Nikitina (Bibl.110) by the reaction:

\[
(CH_3)_3SiCl + BrCH_2CH=CH_2 \rightarrow (CH_3)_2SiCH_2CH=CH_2 + (CH_3)_3SiCH=CHBr
\]

With the purpose of modifying organic resins, S.N. Ushakov (Bibl.111) has proposed the esterification of the free hydroxyl group of resol and novolak resins by means of α- or β-chloroethyltriethylsilane.

**Physical Properties**

The tetraalkyl-substituted silanes with a halogen atom in the organic radical are colorless, very stable liquids, which distil under atmospheric pressure without decomposition. Table 16 gives the principal physical properties of a few organo-silanes containing a halogen atom in the organic radical.
Table 16
Physical Properties of Organo-Substituted Silanes Containing a Halogen in the Organic Radical

<table>
<thead>
<tr>
<th>a) Name; b) Formula; c) Boiling Point, °C; d) Specific Gravity, d_{20}^0; e) Refractive Index, n_{D}^{20}; f) Bibliography</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH_3)_2SiCH_2Cl</td>
</tr>
<tr>
<td>(CH_3)_2SiCH_2J</td>
</tr>
<tr>
<td>(CH_3)_2SiCHCl_2</td>
</tr>
<tr>
<td>(CH_3)_2SiCHClCH_3</td>
</tr>
<tr>
<td>(CH_3)_2SiC_6H_5Br</td>
</tr>
<tr>
<td>(CH_3)_2SiC_6H_4Cl</td>
</tr>
<tr>
<td>(CH_3)_2SiC_6H_4Br</td>
</tr>
<tr>
<td>(CH_3)_2SiC_6H_4Cl</td>
</tr>
<tr>
<td>(CH_3)_2SiC_6H_4Br</td>
</tr>
<tr>
<td>(CH_3)_2SiC_6H_4F</td>
</tr>
<tr>
<td>(CH_3)_2SiC_6H_4Cl</td>
</tr>
<tr>
<td>(CH_3)_2SiC_6H_4Br</td>
</tr>
<tr>
<td>(CH_3)_2SiC_6H_4Cl</td>
</tr>
<tr>
<td>(CH_3)_2SiC_6H_4Br</td>
</tr>
<tr>
<td>(CH_3)_2SiC_6H_4F</td>
</tr>
<tr>
<td>(CH_3)_2SiC_6H_4Br</td>
</tr>
<tr>
<td>(CH_3)_2SiC_6H_4Cl</td>
</tr>
<tr>
<td>(CH_3)_2SiC_6H_4Br</td>
</tr>
<tr>
<td>(CH_3)_2SiC_6H_4Cl</td>
</tr>
<tr>
<td>(CH_3)_2SiC_6H_4Br</td>
</tr>
<tr>
<td>(CH_3)_2SiC_6H_4Cl</td>
</tr>
<tr>
<td>(CH_3)_2SiC_6H_4Br</td>
</tr>
<tr>
<td>(CH_3)_2SiC_6H_4Cl</td>
</tr>
<tr>
<td>(CH_3)_2SiC_6H_4Br</td>
</tr>
<tr>
<td>(CH_3)_2SiC_6H_4Cl</td>
</tr>
<tr>
<td>(CH_3)_2SiC_6H_4Br</td>
</tr>
<tr>
<td>(CH_3)_2SiC_6H_4Cl</td>
</tr>
<tr>
<td>(CH_3)_2SiC_6H_4Br</td>
</tr>
</tbody>
</table>

Chemical Properties

The tetra-substituted silanes with a halogen in the organic radical are stable against water, and possess properties close to those of organic compounds that are
able to form organomagnesium compounds, which makes it possible to obtain from them new compounds with complex organic and organosilicon groups. Thus, under the action of various reagents on bromomagnesiumphenyltriethylsilane, the reactions take place according to the following mechanism (Bibl.112).

\[
\begin{align*}
CH_2CHO + HOH & \rightarrow n-CH_2CH(OH)C_9H_5Si(C_2H_5)_3 \\
C_2H_5CHO + HOH & \rightarrow n-C_2H_5CH(OH)C_9H_5Si(C_2H_5)_3 \\
\cdot BrMgC_9H_5Si(C_2H_5)_3 + C_2H_5CHO + HOH & \rightarrow n-C_9H_5CH(OH)C_9H_5Si(C_2H_5)_3 \\
\cdot BrMgC_9H_5Si(C_2H_5)_3 + HOII & \rightarrow n-BrMgC_9H_5Si(C_2H_5)_3 \\
\cdot BrMgC_9H_5Si(C_2H_5)_3 + C_2H_5CHO + HOH & \rightarrow n-\cdot BrMgC_9H_5Si(C_2H_5)_3 \\
\end{align*}
\]

From the mixed tetra-substituted silanes containing halogen in the organic radical, organosilicon compounds containing atoms of lead, tin, and arsenic have been prepared.

Triethylsilanephenylenetriethylplumbate is obtained as a result of the reaction between trimethylbromoplumbate and triethylmagnesiumbromophenylsilane.

\[
(C_9H_5)_3SiC_9H_5MgBr + (CH_3)_3PbBr \rightarrow (C_9H_5)_3SiC_9H_5Pb(CH_3)_3 \cdot MgBr
\]

Triethylsilanephenylenetriethylplumbate is a colorless thick oil with a faint odor; boiling point 191°C (17 mm); specific gravity \(d_4^{20} = 1.3997\); refractive index \(n_D^{20} = 1.54937\).

Triethylsilanephenylenetriethylstannate is obtained by the reaction of triethylbromostannate with triethylmagnesiumbromophenylsilane:

\[
(C_9H_5)_3SiC_9H_5MgBr + (CH_3)_3SnBr \rightarrow (C_9H_5)_3SiC_9H_5Sn(CH_3)_3 \cdot MgBr
\]

Triethylsilanephenylenetriethylstannate is a colorless, heavy, almost odorless oil; boiling point 214°C (18 mm); specific gravity \(d_4^{20} = 1.1216\); refractive index \(n_D^{20} = 1.52756\).

F-TS-9191/V 196
Triethylsilanephenylenediphenylarsine is obtained by the action of diphenylchloroarsine on triethylbromophenylsilane in the presence of metallic sodium:

\[(\text{C}_2\text{H}_5)_3\text{SiC}_6\text{H}_{4}\text{Br} + \text{C}_6\text{H}_{5}\text{AsC}_2\text{H}_4\text{Na} \rightarrow \text{NaCl} + \text{NaBr} + (\text{C}_2\text{H}_5)_3\text{SiC}_6\text{H}_{4}\text{AsC}_6\text{H}_{4}\text{Na}\]  

Triethylsilanephenylenediphenylarsine is a colorless oil soluble in alcohol and ether; boiling point 279 - 281°C (17 mm); specific gravity \(d_2^{20} = 1.1661\); refractive index \(n_D^{20} = 1.61455\).

The tetra-substituted silanes containing chlorine in the organic radical in the \(\alpha\)-position do not enter into reaction with silver nitrate nor with alkali in aqueous alcoholic and aqueous solutions, but the isomers containing chlorine in the \(\beta\)-position do.

\(\beta\)-Chloroethyltriethylsilane is decomposed on simple boiling, according to the reaction:

\[\text{ClC}_2\text{H}_4\text{Si}(\text{C}_2\text{H}_5)_3 \rightarrow (\text{C}_2\text{H}_5)_3\text{Si} + \text{CH}_2=\text{CH}_2\]

This reaction is accelerated in the presence of AlCl₃.

Compounds in which the chlorine is in the \(\gamma\)-position do not react at all on titration with alkali, but on prolonged reaction with alkali, the cleavage of the chlorine is complete.

It follows from this that compounds containing the C–Cl bond possess a reactivity which varies according to the position of this bond with respect to the silicon atom (Bibl.139). The compounds containing chlorine in the organic radical may be arranged in the following series with respect to their reactivity: the most reactive are the compounds containing the halogen in the \(\beta\)-position, followed by the \(\alpha\)-position, and, last of all, in the \(\gamma\)-position.

In contrast to the \(\alpha\)-chloromethyltrialkylsilanes, the \(\beta\)-chloroalkyltrialkylsilanes are unstable, and even under the action of methyl- or ethylmagnesium bromide undergo quantitative decomposition at the Si–C bond (Bibl.113). A.D.Petrov and
V.F. Mironov, (Bibl.114) however, have shown that in presence of a $\beta$-chloroethyl radical in the compound, only partial cleavage of the organic radical takes place, while the secondary $\beta$-chloroalkyltrialkylsilanes react with $\text{BdG}_X$ without destroying the Si-C bond at all.

They have synthesized a number of compounds by the reaction:

$$(\text{Cl}_3\text{H}_4)_{3}\text{SiCH_2CHBr} + \text{Mg} + \text{C_2H_3Br} \rightarrow (\text{Cl}_3\text{H}_4)_{3}\text{SiCH_2CHC}_2\text{H}_5 + \text{MgBr}$$

$\beta$, $\gamma$-Dihalo-derivatives of the tetraalkylsilanes are easily decomposed on heating according to the reaction:

$$(\text{CH}_3)_2\text{SiCH_2CHICICH}_3 \rightarrow (\text{CH}_3)_2\text{SiCl} + \text{CH_2=CH-CH}_2\text{Cl}$$

An anhydrous solution of sodium iodide reacts with chloro-derivatives and a halogen exchange takes place:

$$(\text{CH}_3)_2\text{SiCH}_2\text{Cl} + \text{NaI} \rightarrow (\text{CH}_3)_2\text{SiCH}_2\text{I} + \text{NaCl}$$

$\alpha$-Chloro-substituted silanes undergo a number of transformations under the action of various reagents, for example:

$$\begin{align*}
(\text{Cl}_3\text{H}_4)_{3}\text{SiCH_2Cl} + \text{AlCl}_3 & \rightarrow (\text{Cl}_3\text{H}_4)_{3}\text{SiCl} \\
(\text{Cl}_3\text{H}_4)_{3}\text{SiCH_2Cl} + \text{RONa} & \rightarrow (\text{Cl}_3\text{H}_4)_{3}\text{SiCH_2OR} \\
(\text{C}_3\text{H}_6)_{3}\text{SiCH_2Cl} + \text{HSCl}_2\text{COOH} & \rightarrow (\text{C}_3\text{H}_6)_{3}\text{SiCH_2SCH_2COOH} \\
(\text{Cl}_3\text{H}_4)_{3}\text{SiCH_2Cl} + \text{ROOC-CH}=\text{CH}_2 & \rightarrow (\text{Cl}_3\text{H}_4)_{3}\text{SiCH_2OCOC_2H}_5 \\
(\text{Cl}_3\text{H}_4)_{3}\text{SiCHCl}-\text{Cl} + \text{KOH} & \rightarrow (\text{Cl}_3\text{H}_4)_{3}\text{SiCH}=\text{CH}_2
\end{align*}$$

**Tetra-Substituted Silanes with an Alcohol Group in the Organic Radical**

The organosilicon compounds whose radicals contain a hydroxyl group cannot be prepared by the ordinary methods of synthesis. Triethylhydroxyethylsilane has been prepared by chlorinating tetraethylsilane, then converting the chloro-derivative
into an acetoxy derivative, and hydrolyzing this derivative:

\[
\text{SiH}_3\text{Cl} \cdot \text{SiH}_3\text{Cl} = (\text{C}_2\text{H}_5)\text{SiC}_2\text{H}_4\text{Cl} \cdot (\text{C}_2\text{H}_5)\text{SiC}_2\text{H}_4\text{OAc} \cdot (\text{C}_2\text{H}_5)\text{SiCH}_2\text{CH}_2\text{OH}
\]

Trimethylhydroxypropylsilane (Bibl.115) has been obtained from chloromethyltrimethylsilane by the action of magnesium on it, followed by the action of acetaldehyde on the organomagnesium compound.

\[
\text{CH}_3\text{SiCH}_2\text{Cl} \cdot \text{Mg} \rightarrow (\text{CH}_3)\text{SiCH}_2\text{MgCl} + \text{CH}_4\text{CHO} \rightarrow (\text{CH}_3)\text{SiCH}_2\text{CH}_2\cdot \text{H}_2\text{O} \rightarrow (\text{CH}_3)\text{SiCH}_2\text{CH}_2\cdot \text{MgClOH} \]

Trimethylhydroxymethylsilane has been prepared in good yield by the following reaction (Bibl.116):

\[
(\text{CH}_3)\text{SiCH}_2\text{Cl} \xrightarrow{\text{KOOAc, HOAc}} (\text{CH}_3)\text{SiCH}_2\text{Cl} \xrightarrow{\text{H}_2\text{SO}_4} \text{MeOH} \xrightarrow{\text{MeOH}} (\text{CH}_3)\text{SiCH}_2\text{OH}
\]

**Preparation of trimethylacetoxymethylsilane.** A mixture of 3.1 mols of chloromethyltrimethylsilane, 3.8 mols of potassium acetate and 420 ml of glacial acetic acid is placed in a rustless steel autoclave and heated for 18 hours at 190 - 192°C. The contents of the autoclave are thoroughly washed with distilled water. The liquid insoluble in the water, after being dried over anhydrous sodium carbonate, takes on a light amber color; its weight is 416.5 g (92%). The mixture is distilled in a column. Almost all of it passes over at 136.2 - 136.8°C (748 mm) and is trimethylacetoxymethylsilane. 5 ml of the product passes over at a higher temperature.

**Preparation of trimethylhydroxymethylsilane.** In 9 mols of absolute methanol, 420 ml (2.5 mols) of trimethylacetoxymethylsilane is dissolved. The solution is acidified with 10 drops of concentrated sulfuric acid. After standing at room temperature for 2 days, 165 ml of an azeotropic mixture of methanol and methylacetate and methyl acetate are distilled from the solution. The residue is diluted
with 4 mols methanol and allowed to stand 4 days at room temperature. Distillation of the reaction mixture yields 268 ml of trimethylhydroxymethylsilane (80%). It has an odor recalling that of methanol.

Organosilicon Y-alcohols with three carbon atoms between the silicon atom and the OH group are prepared by the action of ethylene oxide on the magnesium derivative of trimethylchloromethylsilane.

\[
\begin{align*}
(\text{CH}_3)_3\text{SiCH}_3\text{MgCl} + \text{CH}_2=\text{CH}_2\text{-O} & \rightarrow (\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{OMgCl} \\
(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{OMgCl} + \text{H}_2\text{O} & \rightarrow (\text{CH}_3)_3\text{SiH}_2\text{CH}_2\text{OH} + \text{MgCl}_2
\end{align*}
\]

Since the OH group can be replaced by bromine under the action of PBr\(_3\), it is possible to prepare e-hydroxyamyltrimethylsilane by the successive treatment of \(\gamma\)-hydroxypropyltrimethylsilane with PBr\(_3\), magnesium, ethylene oxide, and, finally, water.

To study the reactivity of trimethylhydroxymethylsilane, Davis and Farnum (Bibl.117) have compared the velocity constants of reaction of equivalent quantities of two alcohols with phenyl isocyanate in benzene solution. They found that on the reaction of the alcohols with phenyl isocyanate, the formation of the corresponding phenylurethane takes place rapidly, irreversibly, completely, and unaccompanied by side reactions. Trimethylhydroxymethylsilane and phenyl isocyanate react according to the formula:

\[
(\text{CH}_3)_3\text{SiOH} + \text{OCON} = \text{H}_2\text{N} \rightarrow \text{C}_6\text{H}_5\text{NHCOOCH}_2\text{Si}(\text{CH}_3)_3
\]

In a vessel with well ground stopper, 1 equivalent of phenyl isocyanate is placed together with 2 equivalents of trimethylhydroxymethylsilane dissolved in 10 ml of dry benzene. The contents of the vessel are allowed to stand for 24 hours at about 25°C. The benzene and the excess of the alcohol are then evaporated off, and the liquid is filtered. The final drying of the precipitate is done under a high vacuum for 24 hours. The product obtained melts at 80 - 80.5°C.
The reaction of neopentyl alcohol with phenol isocyanate was investigated by a similar method. The reaction product melted at 113°C. According to the literature, neopentylphenylurethane melts at 114°C.

For studies by this method, benzene solutions of exactly equivalent quantities of trimethylhydroxymethylsilane and neopentyl alcohol were prepared. In a flask with a glass stopper quantities of each solvent, calculated for the reaction with 1.096 g of phenyl isocyanate, exactly measured from burettes, were mixed. These solutions were rapidly mixed with phenyl isocyanate and allowed to stand at about 25°C for 24 hours. Similar experiments were run with solutions of trimethylhydroxymethylsilane, methanol, and ethanol. The silicon content of the non-volatile reaction products was determined, and the proportion of the silicon derivative participating in the reaction was calculated. The ratios of the velocity constant of the reaction of trimethylhydroxymethylsilane with phenyl isocyanate to the velocity constant of the reaction of the corresponding alcohol with phenyl isocyanate have the following values:

\[ \frac{K_S}{K_{ROH}} = 6.56; \frac{K_S}{K_{CH_3OH}} = 2.9; \frac{K_S}{K_{C,H_4OH}} = 3.57 \]

The relative velocity constant of reaction were calculated by the Davis and Farnum formula, in which \( \frac{K_S}{K_{ROH}} \) represents the ratio of the velocity constant of the reaction of trimethylhydroxymethylsilane with the diisocyanate, to the velocity constant of the reaction with the other alcohol.

A comparison of the velocity constant of the reaction between trimethylhydroxymethylsilane and of several organic alcohols with phenyl isocyanates shows that the reactivity of the organosilicon alcohol is considerably higher than that of the organic alcohols (Bibl.55).
<table>
<thead>
<tr>
<th>Alcohols</th>
<th>Rate of Constant of Reaction of Alcohols with Phenyl Isocyanate</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH₃)₃SiCH₂OH</td>
<td>2.42</td>
</tr>
<tr>
<td>(CH₃)₃CCH₂OH</td>
<td>0.45</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>1.000</td>
</tr>
<tr>
<td>C₂H₅OH</td>
<td>0.82</td>
</tr>
</tbody>
</table>

The high reactivity of trimethylhydroxymethylsilane in the formation of phenylurethane indicates the activating influence of the silicon atom on the O-H bond. The elevated activity of trimethylhydroxymethylsilane may be explained (Bibl.118) by the electronegative nature of the radical (CH₃)₃SiCH₂. It is, however, impossible to explain in this way why benzyl, neopentyl and isobutyl alcohol should have different activities, while the value of the electronegativity of the radicals in them is almost the same. The activity of the alcohols is apparently also affected by their structure.

The alcohols may be arranged in the following series according to their activity:

\[
\text{C}_6\text{H}_5\text{OH} > \text{CH}_3\text{OH} > \text{C}_4\text{H}_9\text{OH} > \text{C}_3\text{H}_7\text{OH} > \text{C}_4\text{H}_10\text{OH} > \text{C}_6\text{H}_{13}\text{CH}_2\text{OH} > \text{C}_6\text{H}_{13}\text{CH} = \text{CH}_2\text{OH} > \text{CH}_3\text{OH} > (\text{CH}_3)_3\text{SiCH}_2\text{OH} 
\]

Organosilicon alcohols are viscous liquids with a number of the properties of organic alcohols. Thus, for example, trimethylhydroxymethylsilane forms very stable sodium and aluminum alcoholates, complex ethers, etc.

At room temperature, sodium slowly dissolves in trimethylhydroxymethylsilane with evolution of hydrogen.
\[2(\text{CH}_3)_3\text{SiCH}_2\text{OH} + 2\text{Na} \rightarrow 2(\text{CH}_3)_3\text{SiCH}_2\text{ONa} + \text{H}_2\]

The organosilicon alcohols behave variously with respect to the action of alkalies. While \((\text{CH}_3)_3\text{SiCH}_2\text{OH}\) and \((\text{CH}_3)_2\text{Si(\text{CH}_2\text{OH})}_2\) are stable compounds, tetramethyl-1,2-(dihydroxymethyl)-disiloxane is readily decomposed under the action of alcoholic solution of an alkali. This same reaction also takes place when the corresponding acetoxy derivatives react with an alkali.

\[\text{KCH}_3\text{COOCH}_2(\text{CH}_3)_2\text{SiOSi}(\text{CH}_3)_2\text{CH}_2\text{OCOC}_2\text{H}_5 \rightarrow 3\text{H}_2\text{O} \rightarrow \]

\[6\text{CH}_3\text{COOC}_2\text{H}_5 + 20(\text{Si}(\text{CH}_3)_2\text{H})\text{O} \rightarrow (\text{Si}(\text{CH}_3)_2\text{H})\text{O} \rightarrow \]

Apparently the group \(-\text{O-Si-C-O-}\), owing to the considerable positive polarization of the silicon atom under the action of the adjoining oxygen atom and carbonyl group, is unstable under the action of nucleophilic agents (OH-groups).

Trimethylhydroxymethylsilane, when dissolved in a boiling 75% solution of KOH, in a few hours forms a transparent solution from which a refractory and easily inflammable gel is separated on the action of acid; trimethylhydroxymethylsilane dissolve pure amalgamated foil very rapidly, with liberation of heat; the reaction is catalytically accelerated by traces of carbon tetrachloride.

When trimethylhydroxymethylsilane is heated with a small amount of metallic sodium in a sealed ampule for 4 days at 175\(^\circ\)C, the trimethylhydroxymethylsilane does not change its properties.

Trimethylhydroxymethylsilane reacts with trimethylchlorosilane as follows:

\[(\text{CH}_3)_3\text{SiCH}_2\text{OH} + \text{ClSi(\text{CH}_3)_3} \rightarrow (\text{CH}_3)_3\text{SiCH}_2\text{OSi(\text{CH}_3)_3} + \text{HCl}\]

**Preparation of hexamethyloxymethylenedisilane.** In a dry solution of quinoline
in chloroform, 19.7 g of trimethylhydroxymethylsilane is dissolved, and, after cooling and vigorous stirring, it is treated with an equivalent quantity of trimethylchlorosilane. The mixture is then vigorously stirred for 5 minutes more, and is then diluted with 250 ml of absolute ether. The quinoline hydrochloride is removed by filtering. Distillation of the filtrate yields 36 ml of hexamethyloxymethylene-disilane; boiling point 129.8°C (738 mm), (in 84% yield).

In 1946 it was found that (CH₃)₃SiCH₂Cl readily forms a Grignard reagent (in 90% yield), which is able to enter into reaction not only with alkyl halides, but also with carbonyl compounds. Under the action of this reagent, for instance, on acetaldehyde, the corresponding secondary alcohol

\[
(CH_3)_3SiCH_2MgCl + CH_3-\overset{\text{C}}{\text{C}}H \rightarrow (CH_3)_3SiCH_2CH_2OH
\]

is obtained. On dehydration of this alcohol, cleavage of the organic radical takes place.

\[
\text{CH}_3\text{CHOHCH}_3 \quad \rightarrow \quad \text{CH}_3\text{CH} = \text{CH}_2
\]

This cleavage is due to the weakness of the Si-C bond in compounds in which functional groups (hydroxyl, halogen, carboxyl) are attached to the β-carbon atom.

On displacement of these functional groups from the β-carbon atom to the Y-atom, the Si-C bond becomes stronger. Thus, the compounds in which hydroxyl and ether groups are attached to the Y-carbon atom have been found to be fairly stable. Compounds of this type have been prepared by the following reactions:

\[
(CH_3)_3SiCH_2MgX + CH_2=O \rightarrow (CH_3)_3SiCH_2CH_2OH
\]

(1)
Table 17 gives the physical properties of tetra-substituted silanes with an alcohol group in the organic radical.

Table 17

Physical Properties of Tetra-Substituted Organosilanes Containing an Alcohol Group in the Radical

<table>
<thead>
<tr>
<th>a) Name</th>
<th>b) Formula</th>
<th>c) Boiling Point, °C</th>
<th>d) Specific Gravity, d_20^0</th>
<th>e) Refractive Index, n_D^20</th>
<th>f) Bibliography</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxymethyltrimethylsilane</td>
<td>HOCH₂Si(CH₃)₃</td>
<td>121.6</td>
<td>0.8261</td>
<td>1.416 (25°)</td>
<td>116</td>
</tr>
<tr>
<td>Hydroxyethyltrimethylsilane</td>
<td>HOCH₂Si(CH₃)₃</td>
<td>115</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydroxyethyltrimethylsilane</td>
<td>HOCH₂Si(CH₃)₃</td>
<td>115</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methylhydroxyphenyltriethylsilane</td>
<td>HO(CH₂)₃Si(CH₃)₃</td>
<td>173-4</td>
<td>0.9596</td>
<td>1.51822</td>
<td>115, 1118</td>
</tr>
<tr>
<td>Ethylhydroxyphenyltriethylsilane</td>
<td>HO(CH₂)₃Si(CH₃)₃</td>
<td>185</td>
<td>0.9575</td>
<td>1.51243</td>
<td>115, 1118</td>
</tr>
<tr>
<td>p-Propylhydroxybenzyltriethylsilane</td>
<td>HO(CH₂)₃Si(CH₃)₃</td>
<td>190-200</td>
<td>0.9491</td>
<td>1.50343</td>
<td>115</td>
</tr>
<tr>
<td>o-Propylhydroxybenzyltriethylsilane</td>
<td>HO(CH₂)₃Si(CH₃)₃</td>
<td>190-200</td>
<td>0.9512</td>
<td>1.51212</td>
<td>115</td>
</tr>
<tr>
<td>Di-(hydroxymethyl)dimethylsilane</td>
<td>(HOCH₂)₂Si(CH₃)₂</td>
<td>130</td>
<td>0.993</td>
<td>1.4611</td>
<td>115</td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Boiling Point, °C; d) Specific Gravity, d_20^0; e) Refractive Index, n_D^20; f) Bibliography
When chloromethyltrimethylsilane reacts with sodium alcoholates, alkoxyethyltrimethylsilanes are formed (Bibl.119):

\[
(CH_3)_3SiCH_2Cl + RONa \rightarrow (CH_3)_3SiOCH_2R + NaCl
\]

Together with this reaction the cleavage of the chloromethyl groups and the formation of hexamethyldisiloxane and methyl chloride also takes place. This side reaction depends on the molecular weight of these alkoxy groups. Methoxymethyltrimethylsilane is prepared in good yield without appreciable cleavage of the chloromethyl group. Ethoxymethyltrimethylsilane is obtained in yield up to 70%, and the cleavage of the chloromethyl group amounts to 11%. Butoxymethyltrimethylsilane is obtained in 19% yield, with the cleavage of the chloromethyl group amounting to 31%.

The silicon content of ethoxymethyltrimethylsilane may be determined by its oxidizing in the presence of water.

**Preparation of methoxymethyltrimethylsilane.** In 40 ml of absolute methanol, 26 g (1.13 mol) of metallic sodium is dissolved. To the solution so obtained 122.5 g (1 mol) of chloromethyltrimethylsilane is added, and the mixture is boiled under a reflex condenser for 24 hours. On completion of the reaction the product is fractionated in a 90 cm column.

The first fraction is an azeotropic mixture of methoxymethyltrimethylsilane and methanol, and boils at 60°C. This fraction, (165 ml), contains 64% of methoxymethyltrimethylsilane.

The second fraction, (85 ml), is collected at 61°C, and is a mixture of methanol, methoxymethyltrimethylsilane and chloromethyltrimethylsilane.

The third fraction, boiling at 64°C, is pure methanol.

No residue of organosilicon compounds is found in the still. The first and second fraction are combined, washed with water to remove the methanol, and again fractionated, giving 114 ml of methoxymethyltrimethylsilane in 75% yield. No phenomena indicating cleavage of the chloromethyl group are observed during the
synthesis.

**Preparation of ethoxymethyltrimethylsilane.** Ethoxymethyltrimethylsilane is prepared from sodium ethylate, but before distillation the mixture is first neutralized with dry HCl, and the NaCl separated is filtered off. Three fractions are obtained on fractionating the reaction products.

The first fraction, (80 ml), boiling at 65.5°C, contains a mixture of trimethylethoxyethylsilane, ethanol, and a certain quantity of unreacted chloromethyltrimethylsilane.

The second fraction (25 ml), boiling at 72°C, is an azeotropic mixture of ethanol and chloromethyltrimethylsilane. It also contains a small amount of ethoxymethyltrimethylsilane.

The third fraction, (205 ml), boils at 74°C, and is an azeotropic mixture of ethoxymethyltrimethylsilane and ethanol. This fraction also contains a certain amount of unreacted chloride.

The further separation of the reaction product proceeds as follows.

The first fraction is treated with dilute HCl. Under this treatment an organic layer separates and is then treated with concentrated sulfuric acid. The part of the liquid that does not dissolve in the sulfuric acid is trimethylchlorosilane. The sulfuric acid is then treated with water, and a small amount of hexamethyldisiloxane is collected.

The second fraction is washed with water, and 56% by volume remains undissolved. The washed organic layer is then treated with cold concentrated sulfuric acid. The part that does not dissolve in the sulfuric acid is chlorotrimethylsilane. The sulfuric-acid layer is then diluted with water. After the dilution an organic layer consisting of ethoxymethyltrimethylsilane is separated.

The third fraction consists mainly of ethoxymethyltrimethylsilane. It is thoroughly washed with water, dried over calcium chloride, and fractionated. The fraction, (101 ml), boiling at 99 - 102°C is ethoxymethyltrimethylsilane with a very
insignificant admixture of chloromethyltrimethylsilane. The product does not change its properties on standing for a few weeks.

Butoxymethyltrimethylsilane is prepared from sodium butylate and chloromethyltrimethylsilane, as methoxymethyltrimethylsilane was prepared, and is separated by fractionating the reaction mixture. The yield does not exceed 20%. The molecular weight of the product cannot be determined by the Meyer method, since when the butoxymethyltrimethylsilane is evaporated in air, strong explosions have been systematically observed. The infrared spectra of all compounds with alkoxy groups in the radicals very much resemble each other and are characterized by an absorption peak at wavelength $1100^{-1}$ cm. This same peak is also characteristic for simple organic ethers.

Ethylcarboxymethyltrimethylsilane has been prepared by the reaction of $[(\text{trimethylsilyl})\text{methyl}]\text{magnesium chloride and ethyl ether with chloroformic acid, by}$ the formula (Bibl.120):

$$\text{(CH}_{3}\text{)}\text{3SiCH}_{2}\text{MgCl} + \text{CH}_{2}\text{CHO} \rightarrow \text{MgCl}_{2} + (\text{CH}_{3}\text{)}\text{3SiCH}_{2}\text{COOC}_{2}\text{H}_{5}$$

Ethylcarboxymethyltrimethylsilane is a colorless liquid with a pleasant fruity odor; it does not react with water. Dilute HCl, alkali, anhydrous HCl, bromine, and absolute ethanol react with ethylcarboxyethyltrimethylsilane according to the following formulas:

$$2\text{(CH}_{3}\text{)}\text{3Si(CH}_{2}\text{COOC}_{2}\text{H}_{5} + \text{HCl}) \rightarrow (\text{CH}_{3}\text{)}\text{3SiOSi(CH}_{3}\text{)}\text{3Si} + 2\text{CH}_{3}\text{COOC}_{2}\text{H}_{5}.$$  
$$\text{(CH}_{3}\text{)}\text{3SiCH}_{2}\text{COOC}_{2}\text{H}_{5} + \text{HCl} \rightarrow (\text{CH}_{3}\text{)}\text{3SiCl} \cdot \text{CH}_{3}\text{COOC}_{2}\text{H}_{5}.$$  
$$\text{(CH}_{3}\text{)}\text{3SiCH}_{2}\text{COOC}_{2}\text{H}_{5} + \text{Br}_{2} \rightarrow (\text{CH}_{3}\text{)}\text{3SiBr} + \text{BrCH}_{2}\text{COOC}_{2}\text{H}_{5}.$$  
$$\text{(CH}_{3}\text{)}\text{3SiCH}_{2}\text{COOC}_{2}\text{H}_{5} + \text{C}_{2}\text{H}_{5}\text{OH} \rightarrow (\text{CH}_{3}\text{)}\text{3Si(OC}_{2}\text{H}_{5}) + \text{CH}_{3}\text{COOC}_{2}\text{H}_{5}.$$  

Preparation of ethylcarboxymethyltrimethylsilane. To 325 g of freshly distilled ethyl ester of chloroformic acid, 1000 ml of dry ether are added. 2 mols
of the Grignard reagent prepared in 95% yield from 2 mols of chloromethyltrimethyl-
silane and 2 gram-atoms of magnesium in 500 mg of dry ether is added gradually.
After introduction of the Grignard reagent into the mixture, it is heated on a water
bath for 5 hours. Owing to the abundant precipitation of magnesium salts, which
makes the stirring difficult, 1000 ml more of ethyl ether must be added. After
standing 12 hours at room temperature, the reaction mixture solidifies, owing to the
formation of etherates of magnesium chloride. The reaction mass is hydrolyzed with
1000 ml of 3% HCl, the ethereal layer is washed with water and dilute sodium carbon-
ate solution and dried over sodium sulfate, and, after distilling off the ether, it
is fractionated on a column with 15 theoretical plates, giving 113.5 g of the ethyl
ester of chloroformic acid, in 25% yield, with a boiling point of 43.5°C (120 mm),
and 239.5 g (1.50 mol) of ethylcarboxymethyltrimethylsilane, with a boiling point of
75.5°C (42 mm) or 157°C (730 mm). Yield, about 75% of theoretical.

Pentamethylchloromethylidisiloxane reacts with potassium acetate in an equal
volume of acetic acid to form pentamethylacetoxyethylidisiloxane, even on simple
heating of the mixture to boiling (Bibl.21). On this reaction, a partial rearrange-
ment of the pentamethylacetoxyethylidisiloxane into hexamethyldisiloxane and
tetramethyl-1,2-di-(acetoxyethyl)-disiloxane is observed:

\[(\text{CH}_3)_5\text{SiOSi(CH}_3)_2\text{CH}_4\text{Cl} + \text{CH}_3\text{COOK} \rightarrow 3\text{KCl} + (\text{CH}_3)_5\text{SiOSi(CH}_3)_2\text{CH}_4\text{OOCCH}_3\]
\[2(\text{CH}_3)_5\text{SiOSi(CH}_3)_2\text{CH}_4\text{OOCCH}_3 \rightarrow (\text{CH}_3)_5\text{SiOSi(CH}_3)_2 + \text{CH}_3\text{COOCH}_2(\text{CH}_3)_5\text{SiOSi(CH}_3)_2\text{CH}_4\text{OOCCH}_3\]

When 1,2-dichloromethyl-1,2-tetramethyldisiloxane reacts with this potassium
acetate under similar conditions, 1,2-diacetoxyethyl-1,2-tetramethyldisiloxane is
formed in quantitative yield.

Acetoxyethylpentamethyldisiloxane and 1,2-dicarboxymethyl-1,2-tetramethyldisiloxane
are stable to the action of aqueous solutions of acids, and are not
hydrolyzed even after 56-hour boiling with 6 N H₂SO₄.
The heating of 1,2-diacetoxymethyltetramethyldisiloxane with 2 N NaOH in 50% ethanol leads to its rapid hydrolysis, forming methyl acetate and hexamethylocyclotrisiloxane.

\[
\begin{align*}
\text{CH}_3\text{OOCCH}_2\text{Si}((\text{CH}_3)_4\text{Si})_3\text{CH} - 2\text{NaOH} \rightarrow & \quad 6\text{CH}_3\text{COOCH}_3 + 2[(\text{CH}_3)_5\text{SiO}]_3
\end{align*}
\]

When 1,2-diacetoxymethyl-1,2-tetramethyldisiloxane reacts with an excess of absolute methanol in the presence of HCl in the cold, 1,2-dihydroxymethyl-1,2-tetramethyldisiloxane is formed in 90% yield. The methyl acetate liberated is distilled off together with the methanol at 53°C, and then the residue is again diluted with methanol to the original volume, and after 24 hours standing, the methanol and methyl acetate are removed under a vacuum at 25°C and 20 mm Hg. The residue is viscous product A. The viscosity at 56°C is 9.1 centistokes, and at 21°C it reaches 32.6 centistokes. Product A forms a di-3,5-dinitrobenzoate with a melting point (crystallized from ethanol) of 118.5 - 119°C. Product A is unstable, and its viscosity increases markedly when heated half an hour at 56°C. When the product is distilled in vacuo at 5 mm, the water is split off and a resin is formed, which, in turn, is again converted into a liquid on treatment with water. The ease of formation of the acetoxy derivatives from chloromethylpentamethyldisiloxane and 1,2-dichloromethyl-1,2-tetramethyldisiloxane is due to the fact that the halogen atom in chloromethylpentamethyldisiloxane is in the α-position with respect to the silicon atom.

The use of acetoacetic ester and its sodium derivative for the synthesis of organosilicon compounds has made it possible to prepare the most varied organic compounds containing the silicon atom. The compounds so prepared have included complex ethers, acids, acid chlorides, ketones, tertiary alcohols, halogen alkyls, and, finally, compounds with several functional groups, for instance keto-ethers.

On the action of sodium-acetoacetic ester on trimethyliodomethylsilane,
β-[ethylcarboxy-(aceto)-]ethyltrimethylsilane is formed. The yield does not exceed 48% of theoretical.

\[
\begin{align*}
(CH_3)_2SiCH_2 & + CH_3COCH_2COCH_3 H_5 \xrightarrow{Na} Na \xrightarrow{CH_3 CO} CH_3 COCH_2COCH_3 H_5 \\
\end{align*}
\]

This compound, on treatment with sodium ethylate, forms an ester, ethylcarboxy-ethyltrimethylsilane, in 64 - 70% yield:

\[
\begin{align*}
(CH_3)_2SiCH_2 & + CH_3COCH_2COCH_3 H_5 + CH_3COONa \xrightarrow{CH_3 CO} CH_3 COCH_2COCH_3 H_5 + CH_3COH \\
\end{align*}
\]

Ethylcarboxyethyl-trimethylsilane is also formed under the action of trimethyl-iodomethylsilane on sodium-acetoacetic ester in the presence of an excess of sodium ethylate.

Ethylcarboxyethyl-trimethylsilane is easily hydrolyzed on heating with dilute aqueous solutions of acids or alkalies; forming carboxyethyltrimethylsilane in 87% yield.

β-[ethylcarboxy-(aceto)]-ethyltrimethylsilane is converted on successive treatment with sodium ethylate and alkyl halides (CH_3I or C_2H_5Br) into β-[ethylcarboxy-(aceto)]-ethyltrimethylsilane (in 58 - 72% yield):

\[
\begin{align*}
(CH_3)_2SiCH_2 & + CH_3COCH_2COCH_3 H_5 + CH_3COONa + (CH_3)_2SiCH_2CH_3 COCH_3 H_5 \xrightarrow{CH_3 CO} \\
\end{align*}
\]

The cleavage of keto-ethers with formation of ketones takes place under the action of concentrated HCl, or (better) of a 10% aqueous NaOH solution. By this method, β-[aceto(alkyl)]-ethylmethysilane (in 81% yield) has been prepared; and

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from β-[ethylcarboxy-(alkyl)-aceto]-ethyltrimethylsilane, there have been prepared
β-[aceto-(methyl)]-ethyltrimethylsilane (53%) and β-[aceto-(ethyl)]-ethyltrimethyl-
silane (20%) by the reaction:

\[
\begin{align*}
&\text{R} - \text{Si} - \text{H} + \text{CH}_3\text{CO} - \text{HO} - \text{H}_2\text{O} \\
&\text{NaOH} \\
&\text{HCl} \\
&\text{Si} - \text{R} - \text{CH}_2\text{CH}_2\text{Si} - \text{H} - \text{CO} - \text{H} - \text{C}_3\text{H}_7\text{OH} \\
&\text{CH}_3\text{CH}_2\text{Si} - \text{R} - \text{CH}_2\text{CH}_2\text{Si} - \text{H} - \text{CO} - \text{H} - \text{C}_3\text{H}_7\text{OH}
\end{align*}
\]

where R = C$_2$H$_5$, CH$_3$ or H.

From the organosilicon ketones formed under the action of organomagnesium com-
pounds, tertiary alcohols are in turn formed. Thus, from acetomethyltrimethylsilane
was prepared β-[hydroxy-(dimethyl)]-ethylmethysilane:

\[
\begin{align*}
&(\text{CH}_3)_2\text{SiCH}_2\text{CO} - \text{H}_2\text{O} + \text{CH}_3\text{MgBr} \\
&\rightarrow (\text{CH}_3)_2\text{SiCH}_2\text{CO} - \text{H}_2\text{O} + \text{MgBr}_2
\end{align*}
\]

From (ethylcarboxyethyl)-trimethylsilane and methylmagnesium bromide was synthesized
γ-[hydroxy-(dimethyl)]-propyltrimethylsilane in yield 63% of theoretical:

\[
\begin{align*}
&(\text{CH}_3)_2\text{SiCH}_2\text{CH}_2\text{CO} - \text{H}_2\text{O} + 2\text{CH}_3\text{MgBr} \\
&\rightarrow (\text{CH}_3)_2\text{SiCH}_2\text{CH}_2\text{CO} - \text{H}_2\text{O} + 2\text{MgBr}_2 \rightarrow (\text{CH}_3)_2\text{SiCH}_2\text{CH}_2\text{CO} - \text{H}_2\text{O} + \text{MgBr}_2
\end{align*}
\]

Under the action of concentrated HCl, the hydroxyl group of γ-[hydroxy-(dimethyl)]-
propyltrimethylsilane is replaced by a halogen atom (in 48% yield). On cautious
oxidation of β-(aceto)-ethyltrimethylsilane by sodium hypobromite in an alkaline
medium, carboxyethyltrimethylsilane (in 41% yield) is formed.

β-[Carboxy(methyl)]-ethyltrimethylsilane is formed on the action of sodium
alcoholate on β-[(ethylcarboxy(methyl)aceto)-ethyltrimethylsilane followed by acid
cleavage by the reaction:
Under the action of thionyl chloride on \(\beta\)-[carboxy(methyl)]-ethyltrimethylsilane, the acid chloride is formed.

\[
(CH_3)_2SiCH_2CHCOOH + SOCl_2 \rightarrow (CH_3)_2SiCH_2COCl + SO_2 + HCl
\]

The corresponding ketones were prepared by the action of dialkyl cadmium compounds on an acid chloride:

\[
2(CH_3)_3SiH_2CHCOCl \cdot R_2Cd \rightarrow 2(CH_3)_3SiH_2CHCOR + CdCl_2
\]

where \(R = CH_3\) or \(C_6H_5\).

Similar substances have been synthesized using phenyldimethyliodomethylsilane \((CH_3)_2(C_6H_5)SiCH_2I\) instead of trimethyliodomethylsilane as the starting substance for the preparation of the ester.

A characteristic feature of compounds containing the keto group is their stability to the action of aqueous solutions of acids and alkalies. Compounds in which the keto group is in the \(\gamma\)-position with respect to the silicon atom are considerably more stable than compounds in which the keto group is in the \(\alpha\) or \(\beta\)-position.

The simple mixed ethers are liquids. Ethoxymethyltrimethylsilane explodes violently on evaporation in a stream of oxygen or air, and also when mixed with
sodium peroxide.

Table 18 gives the properties of the substituted silanes with an ether group in the organic radical.

Table 18

Physical Properties of Substituted Silanes Containing an Ether Group in the Radical

<table>
<thead>
<tr>
<th>a) Name</th>
<th>b) Formula</th>
<th>c) Boiling Point, °C</th>
<th>d) Melting Point, °C</th>
<th>e) Specific Gravity, d⁴₀</th>
<th>f) Refractive Index, n⁺₀</th>
<th>g) Bibliography</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methoxymethyl-trimethylsilane</td>
<td>CH₃OCH₃Si(CH₃)₃</td>
<td>83</td>
<td>--</td>
<td>0.7576</td>
<td>1.3878</td>
<td>119</td>
</tr>
<tr>
<td>Ethoxymethyl-trimethylsilane</td>
<td>CH₂OCH₃Si(CH₃)₃</td>
<td>103</td>
<td>--</td>
<td>0.7555</td>
<td>1.3911</td>
<td>119</td>
</tr>
<tr>
<td>Butoxymethyl-trimethylsilane</td>
<td>CH₃CH₂OCH₂Si(CH₃)₃</td>
<td>150 (751 mm)</td>
<td>--</td>
<td>0.774</td>
<td>1.4038</td>
<td>119</td>
</tr>
<tr>
<td>Acetoxydimethyltrimethylsilane</td>
<td>CH₃COOCH₂Si(CH₃)₃</td>
<td>136.8</td>
<td>--</td>
<td>0.8667</td>
<td>1.4060</td>
<td>118</td>
</tr>
<tr>
<td>Acetoxyethyltrimethylsilane</td>
<td>CH₃COOC₂H₅Si(CH₃)₃</td>
<td>204-214</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>118</td>
</tr>
<tr>
<td>3,5-Dinitrophenylcarboxymethyltrimethylsilane</td>
<td>C₆H₅(NO₂)₂COOCH₂Si(CH₃)₃</td>
<td>70</td>
<td>70.5</td>
<td>--</td>
<td>--</td>
<td>118</td>
</tr>
<tr>
<td>Hexamethyloxymethylmagnesiumsilane</td>
<td>(CH₃)₃SiOCH₃Si(CH₃)₃</td>
<td>121.8</td>
<td>--</td>
<td>0.7781</td>
<td>1.3971</td>
<td>116</td>
</tr>
<tr>
<td>Ethylcarboxymethyltrimethylsilane</td>
<td>C₂H₅COOCH₂Si(CH₃)₃</td>
<td>157.0</td>
<td>(750 mm)</td>
<td>(0.8762)</td>
<td>1.4148</td>
<td>120</td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Boiling Point, °C; d) Melting Point, °C; e) Specific Gravity, d⁴₀; f) Refractive Index, n⁺₀; g) Bibliography

Tetra-Substituted Silanes with a Carboxyl Group in the Organic Radical

Organosilicon compounds containing a carboxyl group in the organic radical may be prepared by various methods. The first compounds of this type were prepared by the action of the ethyl ether of chloroformic acid on trimethylmethylmagnesium-chlorosilane followed by saponification of the ester so obtained:

(CH₃)₂SiCH₂MgCl + C₂H₅COOCH₂ | CH₃COOC₂H₅ |
(CH₃)₂SiCH₂MgCl + MgCl₂ | (CH₃)₂SiCH₂MgCl + H₂O |
(CH₃)₂SiCH₂MgCl + H₂O | (CH₃)₂SiCH₂MgCl + C₂H₅OH |

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The first attempts to separate the carboxymethyltrimethylsilane did not lead to the desired results, since on saponification of the ethyl ester, the destruction of the molecule and cleavage of the organic radical connected with the silicon atom were observed. It is only when the ester is saponified by cold water that the acids can be prepared.

Carboxymethyltrimethylsilane has been synthesized by the action of solid carbon dioxide on trimethylmagnesiumchloromethylsilane, the yield reaching 88% of theoretical.

\[
\text{(CH}_3\text{)}_3\text{Si(CH}_3\text{)}_2\text{MgCl} + \text{CO}_2 \rightarrow \text{(CH}_3\text{)}_3\text{Si(CH}_3\text{)}_2\text{COOMgCl} \xrightarrow{\text{H}_2\text{O}} \text{(CH}_3\text{)}_3\text{Si(CH}_3\text{)}_2\text{COOH} + \text{MgCl}_2
\]

Other compounds have also been prepared by this method (cf. Table 19), such as, for instance, carboxymethylpentamethyldisiloxane and carboxymethyldimethylphenylsilane. They were purified by recrystallization from pantane.

Carboxysthyltrimethylsilane has been prepared from chloromethyltrimethylsilane and acetoacetic ester (in 63% yield), and also form chloromethyltrimethylsilane and malonic ester (in 68% yield). It was purified by distillation in vacuo at 147°C (65 mm).

Table 19 gives the properties of compounds with a carboxyl group in the radical. For comparison we also give, in the same Table, data on a few organic acids.

It will be seen from Table 19 that the presence of silicon lowers the dissociation constant of acids. With increasing length of the carbon chain terminated by the carboxyl group, this influence decreases (Bibl.22).

**Tetra-Substituted Silanes with Nitro and Amino Groups in the Organic Radical**

Only a few representatives of the tetra-substituted silanes with nitro and amino groups in the organic radical are known. The literature describes the preparation of tetra-substituted silanes containing an amino group by reduction of the nitro group, for example, in trimethylnitrophenylsilane (Bibl.123) or by the action
Table 19

Physical Properties of Tetra-Substituted Organosilanes Containing a Carboxyl Group in the Radical (Bibl. 148)

<table>
<thead>
<tr>
<th>a) Name</th>
<th>b) Formula</th>
<th>c) Melting Point, °C</th>
<th>d) Refractive Index, nD</th>
<th>e) Dissociation Constant at 25°C, K = 10^5</th>
<th>f) Ratio of the K of the Acid to the K_1 of Acetic Acid K/K_1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboxymethyltrimethylsilane</td>
<td>(CH₃)₃SiCH₂COOH</td>
<td>40</td>
<td>--</td>
<td>0.60</td>
<td>0.34</td>
</tr>
<tr>
<td>Carboxymethylpentamethyldiisoxane</td>
<td>(CH₃)₂SiOSi(CH₃)₂CH₂COOH</td>
<td>17</td>
<td>1.4149</td>
<td>0.60</td>
<td>0.34</td>
</tr>
<tr>
<td>Carboxymethylidimethylphenylsilane</td>
<td>(C₆H₅)(CH₃)₂SiCH₂COOH</td>
<td>90</td>
<td>--</td>
<td>0.54</td>
<td>0.31</td>
</tr>
<tr>
<td>Carboxyethylidimethylsilane</td>
<td>(CH₃)₂SiCH₂CH₂COOH</td>
<td>22</td>
<td>1.4279</td>
<td>1.24</td>
<td>0.71</td>
</tr>
<tr>
<td>Trimethylpropionic acid</td>
<td>(CH₃)₃C(CH₂COOH)</td>
<td>--</td>
<td>--</td>
<td>1.60</td>
<td>0.46</td>
</tr>
<tr>
<td>Propionic Acid</td>
<td>(CH₃CH₂COOH)</td>
<td>--</td>
<td>--</td>
<td>1.75</td>
<td>0.87</td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Melting Point, °C; d) Refractive Index nD; e) Dissociation Constant at 25°C, K = 10^5; f) Ratio of the K of the Acid to the K_1 of Acetic Acid K/K_1

Table 20

Physical Properties of Tetra-Substituted Organosilanes Containing a Nitro or Amino Group in the Radical

<table>
<thead>
<tr>
<th>a) Name</th>
<th>b) Formula</th>
<th>c) Melting Point, °C</th>
<th>d) Boiling Point, °C</th>
<th>e) Bibliography</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetra-(m-nitrophenyl)trimethylsilane</td>
<td>(NO₂C₆H₅)₂Si</td>
<td>225-226</td>
<td>--</td>
<td>149</td>
</tr>
<tr>
<td>Tetra-(m-aminophenyl)trimethylsilane</td>
<td>(NH₂C₆H₅)₂Si</td>
<td>380</td>
<td>--</td>
<td>350</td>
</tr>
<tr>
<td>p-Nitrophenyltrimethyldiisoxane</td>
<td>(NO₂C₆H₅)₂SiOSi(CH₃)₂</td>
<td>--</td>
<td>140-60</td>
<td>149</td>
</tr>
<tr>
<td>Di-(m-aminophenyl)diethyldiisoxane</td>
<td>(NH₂C₆H₅)₂Si(CH₂)₂Si</td>
<td>89-90</td>
<td>(12-14)</td>
<td>149</td>
</tr>
<tr>
<td>Di-(m-nitrophenyl)diethyldiisoxane</td>
<td>(NO₂C₆H₅)₂Si(CH₂)₂Si</td>
<td>102-103</td>
<td>--</td>
<td>149</td>
</tr>
<tr>
<td>Di-(acetaminophenyl)diethyldiisoxane</td>
<td>(C₆H₅CONHC₆H₅)₂Si(CH₂)₂Si</td>
<td>163-164</td>
<td>--</td>
<td>149</td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Melting Point, °C; d) Boiling Point, °C; e) Bibliography
Table 20 gives the physical properties of tetra-substituted silanes containing a nitro or amino group in the organic radical.

ORGANO-SUBSTITUTED HIGHER SILANES

The higher silanes are unstable substances and have therefore been insufficiently studied. The derivatives of the higher silanes in which only some of the hydrogen atoms have been replaced by organic radicals are also unstable substances. For this reason, down to the present time, such substances as, for example, those of the composition \( \text{H}_5\text{RSi}_2, \text{H}_4\text{R}_2\text{Si}_2, \text{H}_3\text{R}_3\text{Si}_2, \text{etc.}, \) could not yet be prepared. Such derivatives of trisilane, tetrasilane, pentasilane and hexasilane have likewise not been isolated.

On complete replacement of the hydrogen in the higher silanes by organic radicals, more stable substances, which can be isolated by the usual methods, are obtained. Completely substituted higher silanes of the composition \( \text{Si}_2\text{R}_6; \text{Si}_3\text{R}_8; \text{Si}_4\text{R}_{10} \) have been prepared in the pure form, and their properties have been studied; but it has not been possible to isolate completely substituted pentasilanes and hexasilanes in the pure state. There are statements that under the action of metallic sodium on diphenyldichlorosilane, dodecaphenylhexasilane is obtained together with other products, and Kipping (Bibl.125) assigned the formula \( [(\text{C}_6\text{H}_5)\text{Si}]_6 \) to this compound. He also states that from the mucilaginous products obtained on the action of metallic sodium on diphenyldichlorosilane, a mixture of cyclic phenylpolysilanes of composition \( [(\text{C}_6\text{H}_5)\text{Si}]_7 \) and \( [(\text{C}_6\text{H}_5)\text{Si}]_9 \) has been separated. These substances, however, were not isolated in the pure form, and their formulas have not been established.

**Methods of Preparation**

Hexaethylsilane has been obtained by the action of diethylzinc on hexaiodo-silane in a sealed tube.

\[
\text{Si}_2\text{I}_6 + 3\text{Zn}(\text{C}_2\text{H}_4)_2 \rightarrow \text{Si}_6(\text{C}_2\text{H}_4)_6 + 3\text{ZnI}_2
\]
The actual reaction is considerably more complex, and by products are always formed. Their composition has not been studied (Bibl.126). Ipat'ev and Dolgov observed the formation of hexaethyldisilane as a result of the action of hydrogen under pressure on a mixture of tetraethylsilane and phenyltriethylsilane (Bibl.127).

By studying this reaction, Dolgov and Vol'nov (Bibl.128) were able to establish that, when hydrogen under pressure acts at 280 - 300°C on mixed tetra-substituted silanes of the general formula \( R^3SiR \), there is not only the symmetrization reaction characteristic of mixed tetra-substituted compounds, but also another reaction always forming organic derivatives of silane as by products:

\[
R^3SiR + RSiR \quad \text{H}_2 \quad \rightarrow \quad 2RH + R^3SiSiR
\]

By this method they prepared not only hexaethyldisilane but also hexamethyldisilane. Isobutyltriethylsilane, under these conditions, undergoes rearrangement, forming a mixture of various ethyl and butyl-substituted disilanes. They obtained diisobutyltetraethyldisilane and diethyltetraisobutylsilane.

Hexaethyldisilane has been obtained in insignificant quantities by the Grignard reaction (Bibl.120). Hexaphenyldisilane could not be obtained by that reaction. The reaction proceeds with the formation of phenyl-substituted monosilanes (Bibl.129).

The reaction between an alkyl-(aryl)-halosilane and the alkali metals potassium and sodium is of great interest for the preparation of organic derivatives of disilane or the higher silanes. By means of this reaction, a considerable number of substituted polysilanes have been prepared, both with radicals of the same kind and with mixed radicals. Under the action of metallic sodium in xylene solution on triphenylchlorosilane, hexaphenyldisilane has been prepared (Bibl.130):

\[
2\text{C}_6\text{H}_{5}\text{SiCl} + 2\text{Na} \quad \rightarrow \quad 2\text{C}_6\text{H}_{5}\text{SiNa} + 2\text{C}_6\text{H}_{5} + 2\text{NaCl}
\]

By this method, hexabenzyldisilane and mixed derivatives of disilane have been
prepared (Bibl.131). By the action of metallic sodium in aromatic solvents on diphenyldichlorosilane, octaphenylcyclotetrasilane can be obtained:

\[
4(\text{C}_6\text{H}_5)_2\text{SiCl}_2 + 8\text{Na} \rightarrow (\text{C}_6\text{H}_5)_2\text{Si} \bigg(\frac{\text{Si}(\text{C}_6\text{H}_5)_2}{\text{Si}(\text{C}_6\text{H}_5)_2}\bigg) + 8\text{NaCl}
\]

Octatolyltetrasilane and other substituted higher silanes have been prepared by this method (Bibl.132). Together with octaphenylcyclotetrasilane, octaphenyltetrasilane is also formed. The following structure is attributed to it:

\[-(\text{C}_6\text{H}_5)_2\text{Si}((\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_6\text{H}_5)_2)\text{Si}((\text{C}_6\text{H}_5)_2)\text{Si}-\]

Octaphenyltetrasilane is insoluble in the ordinary solvents. According to Kipping, it possesses high activity with respect to the action of chlorine and other halogens. On oxidation it forms a dioxide, to which one of the following structures is attributed:

\[
\begin{align*}
(\text{I}) & \quad (\text{C}_6\text{H}_5)_2\text{Si}((\text{C}_6\text{H}_5)_2 \rightarrow \text{Si}((\text{C}_6\text{H}_5)_2)\text{Si}((\text{C}_6\text{H}_5)_2) \rightarrow \text{Si}(\text{C}_6\text{H}_5)_2) \\
(\text{II}) & \quad (\text{C}_6\text{H}_5)_2\text{Si}((\text{C}_6\text{H}_5)_2)\text{Si}((\text{C}_6\text{H}_5)_2)\text{Si}((\text{C}_6\text{H}_5)_2)
\end{align*}
\]

Under the assumption of formula (I), Kipping postulates the existence of trivalent silicon, which is not very probable, since this compound does not react with hydrogen bromide (Bibl.132). It would be more correct to assume that Kipping had to do with a more complex compound than octaphenyltetrasilane. This is confirmed by the poor solubility of the product under discussion in solvents. The action of various reagents on it, and its high sensitivity to chemical reagents, especially to chlorine, is due to the halogen breaking the Si-Si bond and becoming attached to the silicon.

**Physical Properties**

The substituted higher silanes are rather stable substances and can be
distilled without decomposition. They are liquid or crystalline substances insoluble in water, but readily soluble in such organic substances as benzene, toluene, xylene, dichloroethane, benzine, white spirit, ether, and acetone. They are sparingly soluble in alcohol. Table 21 gives the physical properties of a few representatives of this group of compounds.

Table 21

Physical Properties of Organo-Substitution Products of Higher Silanes

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c) °C</th>
<th>d) °C</th>
<th>e)</th>
<th>f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexamethylsilsilane</td>
<td>(CH₃)₆Si₂</td>
<td>12</td>
<td>112</td>
<td>0.723</td>
<td>128,150</td>
</tr>
<tr>
<td>Hexaethylsilsilane</td>
<td>(C₂H₅)₆Si₂</td>
<td>—</td>
<td>255</td>
<td>0.89/3</td>
<td>120,128,151</td>
</tr>
<tr>
<td>Hexapropylsilane</td>
<td>(C₃H₇)₆Si₂</td>
<td>—</td>
<td>144  (3 mm)</td>
<td>0.869</td>
<td>152</td>
</tr>
<tr>
<td>Diethyl dipropylsilsilane</td>
<td>(C₂H₅)₂(C₃H₇)₂(C₆H₅)₂Si₂</td>
<td>—</td>
<td>270</td>
<td>—</td>
<td>150</td>
</tr>
<tr>
<td>1,1,2-Tetraphenyl-2,2-di-p-tolylsilane</td>
<td>(C₆H₅)₄(C₆H₄CH₃)₂Si₂</td>
<td>220 - 230</td>
<td>(110°)</td>
<td>—</td>
<td>150</td>
</tr>
<tr>
<td>Diethyl dipropylsilsilane</td>
<td>(C₂H₅)₂(C₃H₇)₂(C₆H₅)₂Si₂</td>
<td>—</td>
<td>244</td>
<td>—</td>
<td>159</td>
</tr>
<tr>
<td>Pentaphenyl-p-tolylsilane</td>
<td>(C₆H₅)₅(C₆H₄CH₃)₂Si₂</td>
<td>283 - 295</td>
<td>(20 mm)</td>
<td>—</td>
<td>150</td>
</tr>
<tr>
<td>1,1,2,2-Tetraphenyl-1,2-p-tolylsilane</td>
<td>(C₆H₅)₄(C₆H₄CH₃)₂Si₂</td>
<td>288 - 290</td>
<td>—</td>
<td>—</td>
<td>150</td>
</tr>
<tr>
<td>Hexapropylsilane</td>
<td>(C₃H₇)₆Si₂</td>
<td>—</td>
<td>270</td>
<td>—</td>
<td>150</td>
</tr>
<tr>
<td>1,1,1-Triphenyl-2,2,2-tritolyldisilane</td>
<td>(C₆H₅)₃(C₆H₄CH₃)₂Si₂</td>
<td>352</td>
<td>—</td>
<td>—</td>
<td>130,138</td>
</tr>
<tr>
<td>Hexaethylsilane</td>
<td>(C₂H₅)₆Si₂</td>
<td>262 - 264</td>
<td>—</td>
<td>—</td>
<td>159</td>
</tr>
<tr>
<td>1,2,2-Trityl-1,1,2-triphenylsilane</td>
<td>(C₆H₅)₃(C₆H₄CH₃)₂Si₂</td>
<td>354 - 356</td>
<td>—</td>
<td>—</td>
<td>152</td>
</tr>
<tr>
<td>Hexamethylsilane</td>
<td>(CH₃)₆Si₂</td>
<td>226 - 227</td>
<td>—</td>
<td>—</td>
<td>150</td>
</tr>
<tr>
<td>Octaphenylcyclotetrasilane</td>
<td>(C₆H₅)₆Si₂</td>
<td>194</td>
<td>—</td>
<td>—</td>
<td>152</td>
</tr>
<tr>
<td>1,2-Diphenyl-1,1,2,2-tetraethylsilane</td>
<td>(C₆H₅)₃(C₂H₅)₂Si₂</td>
<td>335</td>
<td>—</td>
<td>—</td>
<td>151</td>
</tr>
<tr>
<td>1,1,2,2-Tetraethylcyclotetrasilane</td>
<td>(C₂H₅)₆Si₂</td>
<td>400</td>
<td>—</td>
<td>—</td>
<td>131</td>
</tr>
<tr>
<td>1,1,2,2,2-Octaphenyltetrasilane</td>
<td>(C₆H₅)₄(C₆H₄CH₃)₄Si₂</td>
<td>240 - 241</td>
<td>—</td>
<td>—</td>
<td>159</td>
</tr>
<tr>
<td>Octa-p-tolylsilane</td>
<td>(C₆H₄CH₃)₆Si₂</td>
<td>293</td>
<td>—</td>
<td>—</td>
<td>132</td>
</tr>
<tr>
<td>Octa-p-tolylcyclotetrasilane</td>
<td>[(C₆H₄CH₃)₆Si₂</td>
<td>310</td>
<td>—</td>
<td>—</td>
<td>154</td>
</tr>
<tr>
<td>Diethyl octaphenyletetrasilane</td>
<td>(C₂H₅)₆(C₆H₅)₂Si₂</td>
<td>254</td>
<td>—</td>
<td>—</td>
<td>153</td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Melting Point, °C; d) Boiling Point, °C; e) Specific Gravity d₂⁰; f) Bibliography

Chemical Properties

The phenyl substitution products of the higher silanes, on heating with water in the presence of piperidine, form diphenylidihydroxsilane:

'F-TS-9191/V 220
\[(C_4H_6)_4Si_4 + 8H_2O \rightarrow 4(C_4H_6)_2Si(OH)_2 + 4H_2\]

This reaction may serve as proof of the structure of cyclooctaphenyltetrasilane. The substitution products of the higher silanes are unstable with respect to the action of air (Bibl.146). When heated in the presence of air, oxidation of the Si-Si bond takes place with formation of the siloxane bond Si-O-Si. The action of alkaline solutions is difficult owing to their poor miscibility with solutions of the substitution products of the higher silanes. Under the action of alkalies in the presence of air, oxidation of the substitution products of the higher silanes takes place, forming siloxanes.

Destructive distillation of octaphenylcyclosilane in the absence of air leads to the formation of tetraphenylsilane, triphenylsilane, and a residue of undestroyed octaphenylcyclotetrasilane.

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CHAPTER IV

ESTERS AND HALO-ESTERS OF ORTHOSILICIC ACID

The compounds in whose molecules the silicon atom is coupled to the organic radicals through oxygen constitute the extensive and rather well studied group of organic esters of the silicic acids.

The contemporary literature manifests a tendency not to include the esters of orthosilicic acid among the true organosilicon compounds, since their molecules do not contain the -Si-O- bond. This fact does undoubtedly set the esters and halo-esters of orthosilicic acid apart as a special type of organic derivatives of silicon. These compounds are of interest today not merely as intermediates in the synthesis of the substituted esters, but also with reference to the direct preparation of polysiloxanes.

We distinguish simple esters of orthosilicic acid, or tetraalkoxy-(tetraaryl-oxo)-silanes, in which the silicon atom is bound to four like alkoxy-(aryloxy) groups, and mixed esters, in which the silicon atom is bound to unlike alkoxy-(aryloxy) groups.

In the molecules of halo-esters, the ether bonds -Si-O-C- are accompanied by -Si-X bonds, X being a halogen atom; thus, in their properties, the halo-esters are a class intermediate between full esters and halo-derivatives of silicon. Among the
halo-esters, simple (with the same kind of alkoxy groups) and mixed halo-esters
(with different alkoxy groups) are distinguished.

ESTERS OF ORTHOSILICIC ACID

Methods of Preparation

Reactions of Esterification of Halosilanes

The principal method of preparing the esters of orthosilicic acid, which is in
widespread use both in laboratory practice and in larger scale operations, is the
reaction between silicon tetrafluoride and alcohols or phenols. The reaction be-
tween SiCl₄ and ethanol is of greatest importance.

The preparation of the ethyl ester of orthosilicic acid — tetraethoxysiloxane
— was described by Ebelman as far back as 1846 (Bibl.1), but the structure of the
silicon derivative so obtained was established only in the middle of the 19th
century by Mendelyev (Bibl.2), who states that this product is a "true neutral
ether of silica*. In 1858 he demonstrated (Bibl.3) that the reaction proceeds
according to the following formula*:

\[
\text{SiCl}_4 + 4\text{C}_2\text{H}_5\text{OH} = \text{Si}((\text{OC}_2\text{H}_5)_4 + 4\text{HCl})
\]

The process of esterification of SiCl₄ by absolute ethanol may be schematically
represented as follows:

\[
\begin{align*}
\text{SiCl}_4 + \text{C}_2\text{H}_5\text{OH} & = \text{Cl}_3\text{SiOC}_2\text{H}_5 + \text{HCl} \\
\text{Cl}_3\text{SiOC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OH} & = \text{Cl}_3\text{Si}((\text{OC}_2\text{H}_5)_4 + \text{HCl} \\
\text{Cl}_3\text{Si}((\text{OC}_2\text{H}_5)_4 + \text{HCl} & = \text{Si}((\text{OC}_2\text{H}_5)_4 + \text{HCl}
\end{align*}
\]

*V.N.Dolgov's monograph (Bibl.4) erroneously states that the structure of
tetraethoxysilane was established by Friedel and Crafts. They published their
papers in 1866 - 1870, while Mendelyev published his in 1858.
A certain quantity of intermediate compounds, with the silicon atom attached to both chlorine and ethoxy groups, is always produced in the process of esterification. Such compounds are called chloro-esters of orthosilicic acid, or alkoxy-chlorosilanes (they are sometimes called "alkyl chlorosilicates"). When SiCl₄ is mixed with alcohol, a complex mixture of products at various stages of esterification is formed. The process is in practice completely irreversible. The course of the reaction represented by the above equations depends on the ratio between the starting reagents, the temperature, the vigor of stirring, and the order in which the components are mixed.

To accomplish the most complete esterification it is advisable to pour the SiCl₄ into the alcohol, taken in slight excess over theoretical (4.2 - 4.4 mols per mol of SiCl₄). In this case a certain excess of alcohol will be maintained in the reaction mixture throughout the entire process. The removal of the HCl from the reaction mixture also favors the completion of esterification. This removal may be accomplished by heating, by aspiration of dry air, or by neutralizing the residues of HCl with sodium ethylate or phosphorus pentoxide (Bibl.5,6,7,8).

**Preparation of the ethyl ester of orthosilicic acid** (Bibl.5). The apparatus used for preparing the ethyl ester of orthosilicic acid consists of a round-bottomed liter flask, provided with a stirrer, a reflux condenser, a thermometer and a dropping funnel, the end of which is lowered to the bottom of the flask. The reflux condenser is connected through a CaCl₂ column to a system assuring the sorption of the HCl liberated during the process of esterification. The flask is cooled from the outside by ice water.

Into the flask 400 g of absolute ethanol is charged, the stirrer is started, and 340 g of SiCl₄ is introduced at a uniform rate through the dropping funnel. The rate is so regulated as to hold the temperature of the mixture in the 20 - 40°C range.

At the beginning of the addition of the SiCl₄ the process is strongly
exothermic, mainly on account of the heat of solution of the HCl in the alcohol. This is confirmed by the fact that when the reaction is run with ethanol which has first been saturated with HCl, the temperature of the mixture does not rise.

After about half of the SiCl₄ has been introduced, the alcohol is saturated with HCl, and the evolution of HCl is intensified.

At this time the source of heat is withdrawn from the reaction mixture.

As long ago as Mendelejev (Bibl.2), it was noted that the liberation of heat in the process of esterification of SiCl₄ could be compensated almost completely by the cooling resulting from the separation of HCl.

If the stirring is vigorous, favoring the evolution of HCl, the mixture temperature may even fall below zero. At this stage of the process it is advisable to heat the mixture to 20 - 40°C.

The introduction of the SiCl₄ is usually prolonged for 4 - 5 hours, after which the mixture temperature is gradually raised to 80°C and held there until no more HCl is evolved. The mass is then cooled and rectified. The tetraethoxysilane is distilled at 166 - 168°C. When absolute ethanol is used, the yield is 70 - 85% of theoretical.

The ratio between the quantity of tetraethoxysilane and that of the high-boiling products in the reaction mixture is determined by the water content of the starting ethanol. Thus, when 92% alcohol is used, the yield of tetraethoxysilane falls to 55% of theoretical.

All investigators have noted the formation of high-boiling products during the synthesis of tetraethoxysilanes. Mendelejev (Bibl.2) was the first to express the opinion that these products consist of polymeric hydrolyzates of tetraethoxysilane, which was later completely confirmed.

The effect of the water content of the alcohol on the yield of the ethyl ester of orthosilicic acid has been shown in detail by me (Bibl.5); it was established in that paper that the yield of ester increases with the concentration of the alcohol.
The formation of high-boiling products has usually been explained by the hydrolysis of the tetraethoxysilane by the moisture, followed by the condensation of the hydrolysis products into polymers. In view of the fact, however, that the rate of hydrolysis of an alkoxy group is much less than the rate of hydrolysis of the Si–Cl group, this explanation is not very plausible. It seems to me that it would be more correct to suppose that on the introduction of the SiCl₄ into the mixture of alcohol and water, parallel to the main reaction of esterification of the SiCl₄, the partial hydrolysis of the SiCl₄ and the condensation of the hydrolyzates to polychlorosiloxanes also take place:

\[
\text{SiCl}_4 + \text{H}_2\text{O} \rightarrow \text{Cl}_3\text{SiOH} + \text{HCl}
\]

\[
2\text{Cl}_3\text{SiOH} = \text{Cl}_3\text{SiOSiCl}_3 + \text{H}_2\text{O} \text{ etc.}
\]

or that there is hydrolysis of the halo-esters formed in the initial stage of esterification, and condensation of the products of hydrolysis, forming polyethoxychlorosiloxanes:

\[
\text{C}_3\text{H}_2\text{OSiCl}_4 + \text{H}_2\text{O} = \text{C}_3\text{H}_2\text{OSiCl}_2\text{OH} + \text{HCl}
\]

\[
2\text{C}_3\text{H}_2\text{OSiCl}_2\text{OH} = \text{C}_3\text{H}_2\text{OSiCl}_2\text{OSiCl}_2\text{OC}_2\text{H}_5 + \text{H}_2\text{O}
\]

\[
\text{C}_3\text{H}_2\text{OSiCl}_2\text{OSiCl}_2\text{OC}_2\text{H}_5 + \text{H}_2\text{O} = \text{C}_3\text{H}_2\text{OSiCl}_2\text{OSiCl}_2\text{OH} + \text{C}_2\text{H}_5\text{OSiCl}_2\text{OSiCl}_2\text{OC}_2\text{H}_5 + \text{HCl}
\]

\[
\text{C}_3\text{H}_2\text{OSiCl}_2\text{OSiCl}_2\text{OC}_2\text{H}_5 + \text{HOSiCl}_2\text{OC}_2\text{H}_5 = \]

\[
= \text{C}_3\text{H}_2\text{OSiCl}_2\text{OSiCl}_2\text{OC}_2\text{H}_5\text{OSiCl}_2\text{OC}_2\text{H}_5 + \text{H}_2\text{O} \text{ etc.}
\]

In connection with the processes of hydrolysis, the quantity of water in the
reaction mixture decreases, and the reaction is gradually directed toward esterification, at first of the SiCl₄, later of the polychlorosiloxanes and polyethoxy-
chlorosiloxanes to form both tetraethoxysilane and polyethoxysiloxanes.

Hydrolytic processes may also occur during the stage of warming up and
removal of the HCl. In the cold, the process of condensation of the intermediate
products of hydrolysis does not proceed to completion, but on heating the condensa-
tion is more complete, and in this case water is split off:

\[
\begin{align*}
\text{Si}-\text{Cl} + \text{HO}-\text{Si} & \rightarrow \text{Si}-\text{O}-\text{Si} + \text{HCl} \\
\text{H}_2\text{O} & \rightarrow \text{H}_2\text{O}
\end{align*}
\]

The water first hydrolyzes the -Si-Cl bonds, and then the -Si-OC bonds as well.

When SiCl₄ reacts with ethanol containing more than 8% of water, coagulation of the
reaction mass is, as a rule, observed, in connection with these processes of hydrol-
ysis. The processes of esterification of SiCl₄ are still further complicated by the
additional formation of water on account of the side reaction between the alcohol
with the HCl liberated:

\[
\text{C}_2\text{H}_5\text{OH} + \text{HCl} = \text{C}_2\text{H}_5\text{Cl} + \text{H}_2\text{O}
\]

When SiCl₄ reacts with ethanol, this side reaction does not exert a substantial in-
fluence on the course of the process, but in the reaction with methanol it does
play a great role. Thus, in performing the process by the same method as used in
the synthesis of tetraethoxysilane, only polymethoxysilanes are formed instead of
tetramethoxysilane. Even when absolute alcohol is used, the reaction mixture often
coagulates. The esterification of SiCl₄ by methanol takes place considerably fast-
er than by ethanol, and therefore the synthesis of tetramethoxysilane is usually
performed by rapidly pouring SiCl₄ into methanol, taken in slight excess (5%).
followed by the immediate driving off of the HCl and the unreacted methanol (Bibl.9). The yield of tetramethoxysilane in this case amounts to 60 - 80% of the theoretical. According to Kalinin (Bibl.10), the synthesis is facilitated by using benzene as a solvent, adding it in equal volumes to the alcohol and to the SiCl₄. The yield of tetramethoxysilane by this method is 73% of theoretical. The yields of tetraethoxy-, tetrabutoxy-, tetraisobutoxy- and tetraisoamyloxysilane are 87, 82.5, 81.6 and 79% respectively.

According to Kreshkov and Nessonova (Bibl.11), both the ethyl and methyl esters of orthosilicic acid may be obtained when the reaction mixture is cooled with solid carbon dioxide. The HCl is removed from the reaction mixture by aspirating dry air through it. The yield of the products in this case, however, is not increased; thus tetramethoxysilane is obtained in yield of 67.3% of theoretical, and tetraethoxysilane 79.3% of theoretical.

The esterification of SiCl₄ by allyl alcohol is performed by the same technique as that of methanol, at low temperature, followed by rapid distillation.

The butyl and isobutyl esters of orthosilicic acid have been synthesized by me by the method described for the synthesis of the ethyl ester (Bibl.5). For the completion of the reaction I recommend heating the product of esterification to a temperature of about 150°C. A more convenient method of synthesizing the esters of the higher alcohols is the alcoholysis of the lower esters. The velocity of the esterification reaction of SiCl₄ by phenols is considerably lower than that of the aliphatic alcohols, and a prolonged heating at high temperature is necessary to complete the process (Bibl.12).

Preparation of tetraphenoxysilane. In a retort provided with a reflux condenser, 100 g of phenol is placed and 30 g of SiCl₄ is added. When these reagents are mixed, no HCl is evolved. The signs of a reaction occurring can be observed only after 1 to 2 hours (at 120°C). The evolution of HCl is accompanied by a lowering of the temperature, and if the mixture is not heated, it stops after 10 to 12 hours.
The temperature of the mixture is then raised to 60°C and maintained at this level for 4 - 5 hours, after which it is then gradually raised to 220 - 250°C. After maintaining this temperature for 3 to 4 hours, the evolution of HCl is completed. The mixture is now distilled. The excess of phenol passes over up to 250°C, the chloro-esters at 250 - 270°C, and the tetraphenoxy silane at 415 - 440°C. On redistillation, the tetraphenoxy silane boils at 417 - 420°C. It is a syrupy liquid, which crystallizes when cooled to 0°C. Recrystallization from a mixture of benzene and petroleum ether yields crystals of the melting point 47 - 48°C. The yield of the product is 78% of theoretical. In this way a number of aromatic esters of orthosilicic acid were prepared, including the esters of phenols containing a second hydroxyl group, for example carvacrol and guaiacol (Bibl.13).

The preparation of mixed esters of orthosilicic acid is usually performed in two stages:

1. Synthesis of the alkoxyhalosilane from SiCl₄ and the alcohol:

   \[ \text{SiCl}_4 + x\text{ROH} = (\text{RO})_x\text{SiCl}_{4-x} + x\text{HCl} \]

2. Esterification of the alkoxyhalosilane by a different alcohol:

   \[ (\text{RO})_x\text{SiCl}_{4-x} + (4-x)\text{R"OH} = (\text{RO})_x\text{Si(OR")}_4-x + (4-x)\text{HCl} \]

A number of alkylalkylene esters of orthosilicic acid were prepared by this method (Bibl.12).

Preparation of diallyloxydiethoxysilane. To a mixture of 56.7 g of diethoxydichlorosilane and 52.2 g of anhydrous pyridine, cooled in an ice bath, 38.3 g of allyl alcohol is gradually added. The reaction product is rapidly washed for several times with cold water, dried over calcium chloride, and distilled in vacuo. The yield is 72 - 80% of theoretical. By a similar method the same product may be obtained by esterification of diallyloxydichlorosilane by ethanol. The yield is 70% of theoretical.
Esters of orthosilicic acid may be prepared by the reaction of SiCl₄ with esters of nitrous acid (Bibl.14).

\[
\text{SiCl}_4 + 4\text{CH}_3\text{ONO} = \text{Si(OCH}_3\text{)}_4 + 4\text{NOCl}
\]

The reaction is completed in the cold, and the nitrosyl chloride is then removed by heating. The process proceeds more smoothly and with better yield if it is run in a medium of neutral solvent, for instance in benzene (Bibl.15). Tetramethoxysilane is obtained in this way in yield of 80% of theoretical.

The esterification of SiCl₄ may also be conducted by the action of ethylene oxide (Bibl.16); in this case esters with halogen in the organic radical are formed:

\[
\text{SiCl}_4 + 4\text{CH}_2\text{CH}_2\text{O} = \text{Si(OCH}_3\text{CH}_2\text{Cl)}_4
\]

A substantial advantage of this process is that HCl is not evolved. It is believed that in the first phase of the reaction the HCl dissolves in the SiCl₄ combined with the ethylene oxide:

\[
\text{CH}_2\text{CH}_2\text{O} + \text{HCl} = \text{HOCH}_2\text{CH}_2\text{Cl}
\]

In the second stage, the HCl is regenerated:

\[
\text{SiCl}_4 + 4\text{HOCH}_2\text{CH}_2\text{Cl} = \text{Si(OCH}_3\text{Cl)}_4 + 4\text{HCl}
\]

The ethylene oxide may either be pumped into the autoclave together with the SiCl₄ under a pressure of 1 - 1.1 atm, or may be passed in in the form of bubbles at the boiling point of SiCl₄. The yield of tetra-β-chloroethoxysilane amounts to 70 - 90% of theoretical.

An ester isomeric with tetraallyloxysilane may be prepared from acetone and SiCl₄ (Bibl.17). On reaction with metallic sodium, acetone forms acetone alcoholate (phenol form) CH₂ = C(CH₃)ONa, which reacts with SiCl₄ to yield the ester of
orthosilicic acid:

$$\text{SiCl}_4 + 4\text{CH}_3\text{CONa} = \text{Si(OC} = \text{CH}_3)_4 + 4\text{NaCl}$$

When $\text{SiCl}_4$ reacts with organic acids, mixed anhydrides of orthosilicic acid may be obtained:

$$\text{SiCl}_4 + 4\text{RCOOH} = \text{Si(OCOR)}_4 + 4\text{HCl}$$

K.D. Petrov (Bibl.18) has prepared the most interesting representative of this class of compound, silicoformic anhydride.

**Preparation of silicoformic anhydride.** To a solution of 92 g of formic acid in 150 ml of benzene, under stirring and cooling, 85 g of $\text{SiCl}_4$ are poured. The mixture is heated to 60°C on a water bath until the evolution of HCl stops, and then for 1 hour on a boiling water bath. The benzene is distilled off and then, under reduced pressure of 20 mm, the unreacted formic acid. The residue in the flask is silicoformic anhydride contaminated by the products of its partial decomposition, which are siloxanes of the following structure (Bibl.19):

$$\left(\begin{array}{c} \text{H} \\ \text{C} \\ \text{O} \end{array}\right) \text{Si}\left(\begin{array}{c} \text{OSi} \\ \text{OC} = \text{H} \end{array}\right)_{1,1} \text{OC} = \text{H}$$

The product so obtained can be used for the synthesis of aromatic aldehydes and esters of formic acid.

By the same reaction as $\text{SiCl}_4$, the other chlorosilanes and oxychlorosilanes also react with alcohols and phenols. The reaction of an aliphatic alcohol with trichlorosilane (Bibl.20) may take place either with formation of a trialkylsiloxane $\text{HSi(OR)}_3$ or a tetraalkoxyxilane. The velocity of the second reaction, in which cleavage of the $\text{-Si-H}$ bond occurs, decreases at a low temperature, even when a
solvent is used, and also decreases with increasing molecular weight of the alcohol. When 72 ml of absolute ethanol is added to 25 ml of trichlorosilane at a temperature of 0°C, the reaction product will contain only tetraethoxysilane (14 g). If at the same temperature, 35 ml of ethanol is added to 15 ml of trichlorosilane dissolved in 50 ml of benzene, and the mixture is held at 0°C for 2 hours, the reaction product will contain 12 g of triethoxysilane and 3 g of tetraethoxysilane (Bibl.20). From butyl alcohol, in the absence of a solvent, 16% of tributoxysilane and 32% tetrabutoxysilane is formed, while in a solvent it is 71% of tributoxysilane and 7% of tetrabutoxysilane that are formed.

On heating hexachlorodisilane (Bibl.21) with ethanol, hexaethoxysilane in 25% yield is formed; the reaction with propyl alcohol leads to the formation mainly of tetrapropoxysilane with 12% of hexapropoxydisilane.

The reaction of esterification of polychlorosiloxanes takes place at a relatively lower velocity than the reaction of esterification of \( \text{SiCl}_4 \), and it requires higher temperatures for its completion. The process with ethanol is conducted with the removal of the HCl by a current of nitrogen (Bibl.22), otherwise the prolonged heating of the mixture will lead to its hydrolysis on account of the water formed by the reaction of the alcohol with HCl. In this way a number of polyethoxysiloxanes, up to hexasiloxane, were prepared. The reaction velocity depends to a considerably greater extent on the number of silicon atoms in the siloxane chain than on the molecular weight or the structure of the alcohol. Thus, to complete the reaction:

\[
\text{Si}_4\text{O}_2\text{Cl}_{16} + 14\text{C}_2\text{H}_5\text{OH} \rightarrow \text{Si}_4\text{O}_3(\text{OC}_2\text{H}_5)_{14} + 14\text{HCl}
\]

the reaction mixture must be heated to 160°C, while hexachlorodisiloxane can be esterified by cyclohexanol at a lower temperature.

When a mixture of 11 g of hexachlorodisiloxane, 50 ml of ethyl ether, and 27 g of cyclohexanol is boiled for 8 hours, hexacyclohexyloxydisiloxane is formed (Bibl.23) as crystals with a melting point, after recrystallization from benzene and
dioxane, is 217.1 - 217.6°C.

It is commonly known that the phenols give practically no reaction with HCl, and therefore the esterification of polychlorosiloxanes by phenols can be accomplished without taking special measures of precaution against the action of HCl (Bibl.24). The mixture of polychlorosiloxanes obtained by the reaction of silicon with a mixture of chlorine and oxygen is heated with twice the amount of phenol. The reaction of esterification is completed at a temperature of about 200°C, and then, on heating up to 500°C, the polyphenylsiloxanes are distilled off. A study of the reaction product shows that they consist of linear polyphenoxysiloxanes up to heptasiloxane; in addition, the presence of octaphenoxycyclotetraphenoxane has been established.

The papers (Bibl.21) pointing to the formation of considerable quantities of tetraalkoxysilanes on the esterification of hexachlorodisiloxane are of very great theoretical interest. Thus, for example, when 50 ml of propyl alcohol is heated with 20 ml of hexachlorodisiloxane at 120°C until the evolution of HCl stops, a mixture is obtained which, on rectification in vacuo, yields 6 g of tetrapropoxsilane of boiling point 125 - 130°C (25 mm) and 8.5 g of hexapropoxydisiloxane, with a boiling point of 205 - 208°C (25 mm).

The HCl liberated during the reaction probably catalyzes, at a high temperature, the process of rearrangement of the siloxane bonds, leading to the formation of tetraalkoxysilanes and high-molecular products by the following reaction:

\[ 2CH_3SiOSiCl_2 + 4EX_2 + H_2O \rightarrow SiOCH_3SiOCH_3 + 4SiCl_4 \]

On esterification of bromo- and iodosiloxanes, the side reaction between the hydrogen halide and the alcohol is of far greater importance than in the esterification of chlorosiloxanes. Thus, for example, on the esterification of polybromosiloxane by ethanol, only higher polyethoxysiloxanes and ethyl bromide are formed. An ester with the same number of siloxane bonds as the original polybromosiloxane may be
obtained from the latter compound only by the action of sodium ethylate (Bibl.22).

The reaction of $\text{SiCl}_4$ with alcohols does not lead to the formation of esters of orthosilicic acid; the esterification of $\text{SiI}_4$ may be accomplished by the mere action of ether (Bibl.25):

$$\text{SiJ}_4 + 4(\text{C}_2\text{H}_5)_2\text{O} \rightarrow \text{Si}(\text{OC}_2\text{H}_5)_4 + 4\text{C}_2\text{H}_5\text{J}$$

Reactions of Alcoholysis

The most convenient method of obtaining the higher esters of orthosilicic acids from high-boiling alcohols, as well as from other hydroxyl-containing organic compounds, is the reaction of the lower esters, tetramethoxysilane and tetraethoxysilane with higher alcohols and other compounds containing the hydroxyl groups. The reaction of alcoholysis is more applicable for the preparation of the higher esters than the reaction of esterification, owing to the fact that the evolution of HCl in the process of esterification lead to a number of side reactions, for instance the formation of water, the redistribution of the alkoxy groups in the preparation of mixed esters, etc. It is, moreover, not always convenient to conduct a reaction with such a volatile reagent and $\text{SiCl}_4$.

The lower esters of orthosilicic acid enter most readily into the reaction of alcoholysis with alcohols of higher molecular weight than their alkoxy group. With alcohols of smaller molecular weight than the alkoxy group of the esters, the reaction of alcoholysis is difficult. In the absence of catalysts, tetraethoxysilane enters into reaction with methanol (Bibl.26) only at the temperature of 210°C:

$$\text{Si}(\text{OC}_2\text{H}_5)_4 + 2\text{CH}_3\text{OH} \rightarrow (\text{C}_2\text{H}_5\text{O})_2\text{Si}(\text{OC}_2\text{H}_5)_2 + 2\text{C}_2\text{H}_5\text{OH}$$

At the boiling point, tetramethoxysilane does not react with the higher alcohols unless catalysts are used. When they are used (dry HCl, $\text{SiCl}_4$) (Bibl.27), and also metallic sodium or sodium methylate (Bibl.28), the process proceeds smoothly, and, as a rule, with good yield.
The reaction of alcoholysis is usually run in a flask serving as the still of a rectification column, and the alcohol liberated during the reaction is distilled off. A few examples of the conduct of the alcoholysis reaction are given below (Bibl.29).

Preparation of alkoxy silanes. 1. A mixture of 208 g of tetraethoxysilane, 255 g of allyl alcohol, and 1 g of SiCl₄, is heated in a flask with a column (reflux ratio 5:1) until the liberation of ethanol ceases (20 hours). Rectification of the reaction product yields tetraallyloxysilane. The yield is 91% of theoretical.

2. A mixture of 417 g of tetraethoxysilane and 232 g of allyl alcohol is heated for 8 1/2 hours, distilling off the ethyl alcohol formed. During this period 1 drop of SiCl₄ is added to the reaction mixture every half hour. Rectification of the reaction product yields 0.117 mol of tetraethoxysilane, 0.434 mol of allyloxytriethoxysilane, 0.537 mol of diallyloxydiethoxysilane, and 0.0092 gram-mol of tetraallyloxysilane.

3. As a result of the reaction of equimolecular quantities of tetraethoxysilane and cyclohexanol, a mixture of cyclohexyloxysthoxysilanes and tetracyclohexylloxysilane (39%) and ethanol is formed. On the reaction of equimolecular quantities of tetraethoxysilane and methallyl alcohol, a mixture of methallyloxyethoxysilanes and tetramethallyloxysilane (52%) is formed. When tetraethoxysilane reacts with crotlyl alcohol, tetracrotloyloxysilane (75%) is formed.

4. The reactions of alcoholysis of tetramethoxysilane proceed as easily; thus, the reaction of 137 g of tetramethoxysilane and 130 g of methallyl alcohol (130 g) leads to the formation of (0.196 mol) of dimethoxydimethallyloxysilane, (0.6 mol) of methoxytrimethallyloxysilane, and (0.127 mol) of tetramethallyloxysilane. In this reaction, 0.0039 mol of tetramethoxysilane remains unreacted. On the reaction of tetramethoxysilane with allyl alcohol, methoxyallyloxysilanes are obtained.

5. Distillation of a mixture of 1 mol of tetramethoxysilane with 5 mols of propyl alcohol in the presence of 0.01 mol of sodium alcooholate (Bibl.12) yields
tetrapropoxysilane in 80% yield. Tetrabutoxysilane can be obtained in the same yield by a similar method; tetraisobutoxysilane is obtained in 32% yield. When tetraethoxysilane is heated with stearyl, oleyl or linoleyl alcohols in the presence of sodium alcoholate, the corresponding esters of orthosilicic acid are obtained (Bibl.30).

6. When a mixture of 9.2 g of tetraethoxysilane, 0.2 g of sodium methyleate, and 50 g of stearyl alcohol is heated for 6 hours in a current of carbon dioxide gas, removing the ethyl alcohol through a rectification column, stearyl ether with an admixture of tetraethoxysilane and intermediate products of alcoholysis is obtained. The by products are removed by distillation to 80°C at a residual pressure of 15 mm. The residue is tetrastearyloxysilane. Its yield is 42 g, or 84% of theoretical; on cooling to 0°C it crystallizes, and after recrystallization from methanol and ligroin, it has a melting point of 55.8 - 56.2°C.

When tetraphenoxy silane is heated in a sealed tube with ethanol at 180 - 200°C, tetraethoxysilane, phenol, and a mixture of phenoxyethoxysilanes are obtained (Bibl.13).

\[
\text{Si(OCH}_3\text{II}_4 + 4\text{C}_4\text{H}_8\text{OH} \rightarrow \text{Si(OCH}_3\text{I}_4 \cdot 4\text{C}_4\text{H}_8\text{OH}}
\]

\[
2\text{Si(OCH}_3\text{II}_4 + 3\text{C}_3\text{H}_7\text{OH} \rightarrow \text{Si(OCH}_3\text{I}_4 \cdot (\text{OC}_3\text{H}_7\text{II}_3) \cdot \text{Si(OCH}_3\text{I}_4 \cdot 3\text{C}_4\text{H}_8\text{OH}}
\]

The substitution of ethoxy groups for the phenoxy groups indicates the high stability of the bonds between the ethoxy group and the silicon atom.

On alcoholysis of tetraethoxysilane by menthol (Bibl.31), mono- and dimethoxystri- and diethoxysilanes were obtained (Bibl.31):

\[
\text{Si(OCH}_3\text{II}_4 + \text{C}_{16}\text{H}_{33}\text{OH} = \text{Si(OCH}_3\text{I}_4 \cdot (\text{OC}_3\text{H}_7\text{II}_3) + \text{C}_4\text{H}_8\text{OH}}
\]

\[
\text{Si(OCH}_3\text{I}_4 \cdot (\text{OC}_3\text{H}_7\text{II}_3) + \text{C}_{16}\text{H}_{33}\text{OH} = \text{Si(OCH}_3\text{I}_4 \cdot 2\cdot (\text{OC}_3\text{H}_7\text{II}_3) + \text{C}_4\text{H}_8\text{OH}}
\]

Organic acids (Bibl.32) may enter into the reaction as the alcohols do:
Si(OC\(_2\)H\(_4\))\(_4\) + CH\(_2\)=CHOHCH\(_2\)OH → Si(OC\(_2\)H\(_4\))\(_4\) + CH\(_2\)=CHOHCH\(_2\)OH

the esters of oxy-acids can also behave in this way (Bibl. 33), for instance the ethyl ester of lactic acid:

\[
\text{Si(OC}_2\text{H}_4\text{)}\text{4} + 2\text{HOCHCH}_2\text{OCOC}_2\text{H}_2\text{Cl} \rightarrow \text{Si(OC}_2\text{H}_4\text{)}\text{4} + 2\text{C}_2\text{H}_4\text{OH}
\]

or of ricinoleic acid:

\[
\text{Si(OC}_2\text{H}_4\text{)}\text{4} + 2\text{C}_2\text{H}_5\text{CH}2\text{OHCH}_4\text{OH} \rightarrow \text{Si(OC}_2\text{H}_4\text{)}\text{4} + 2\text{C}_2\text{H}_5\text{OH}
\]

The reaction of alcoholysis of alkoxysilanes may also be conducted by the action of polyhydric alcohols (Bibl. 34) or of their partial esters (Bibl. 21). Thus, tetra-β-methoxyethoxysilane is obtained on heating a mixture of 1 mol of tetraethoxysilane and 5 mols of the monomethyl ester of glycol:

\[
\text{Si(OC}_2\text{H}_4\text{)}\text{4} + 4\text{HOCH}_2\text{H}_4\text{OCH}_2\text{H}_4\text{O} \rightarrow \text{Si(OC}_2\text{H}_4\text{)}\text{4} + 4\text{C}_2\text{H}_4\text{OH}
\]

Tetra-β-ethoxyethoxysilane (yield 94\% of theoretical), and tetra-β-phenoxyethoxysilane may be obtained similarly. Monoglycerides (Bibl. 35), for instance glyceryl acetate, the monoglyceride of linseed oil or cottonseed oil, glyceryl-ethyl ether, as well as diglycerides, may enter into the reaction of alcoholysis. The following reactions are described in the literature (Bibl. 36):

\[
\text{Si(OC}_2\text{H}_4\text{)}\text{4} + 4\text{HOCH}_2\text{H}_4\text{OHCH}_2\text{OCOR} = \text{Si(OC}_2\text{H}_4\text{)}\text{4} + 4\text{C}_2\text{H}_4\text{OH}
\]

\[
\text{Si(OC}_2\text{H}_4\text{)}\text{4} + 4\text{HOCH}_2\text{H}_4\text{OCH}_2\text{OR} = \text{Si(OC}_2\text{H}_4\text{)}\text{4} + 4\text{C}_2\text{H}_4\text{OH}
\]

where \( R = \text{C}_3\text{H}_7 \) and \( \text{C}_{17}\text{H}_{35} \). The process is conducted in an autoclave at a temperature of 150 - 160°C. The author states that β-hydroxyglycerol does not enter into the reaction of alcoholysis.

Alcoholysis and reesterification may also occur under the influence of the free
hydroxyl and carboxyl groups in the condensation products of polybasic acids and polyhydric alcohols (Bibl.35). The reaction of alcoholysis may take place with the most varied alcohols and phenols having a second functional group, for instance with the aminophenols (Bibl.37).

\[ \text{Si(OC}_2\text{H}_5)_4 + 4\text{HOC}_6\text{H}_4\text{NH}_2 = \text{Si(OC}_6\text{H}_4\text{NH})_4 + 4\text{C}_2\text{H}_5\text{OH} \]

The reaction of alcoholysis is characteristic not only for the esters of orthosilicic acid, but for most other compounds containing the \(-\text{Si-O-}\) bond, for example, for the substituted esters and their alkoxy silanes (Bibl.27).

\[
(\text{C}_2\text{H}_5\text{O})_3\text{SiOSi(OC}_2\text{H}_5)_3 + 6\text{CH}_2=\text{CCH}_3\text{OH} \rightarrow \rightarrow \rightarrow
(\text{CH}_2=\text{CCH}_3\text{O})_3\text{SiOSi(OCH}_2\text{CCH}_2=\text{CH})_3 + 6\text{C}_2\text{H}_5\text{OH}.
\]

This reaction takes place on heating a mixture of 34.2 g of hexaethoxydisiloxane and 86 g of methallyl alcohol for 3 hours at boiling point. The yield of hexamethallyloxydisiloxane is 50%.

It has been stated above that the tetramethoxysilane and tetraethoxysilane enter most readily into the reaction of alcoholysis. However, when catalysts are used, the more complex esters, up to tetraamylxysilane and tetraallyloxysilane (Bibl.27), may also be made to react.

The Reesterification Reaction

The reaction of tetraalkoxysilanes with complex esters (reesterification reaction) proceeds easily only in the presence of catalysts, the alcoholates of magnesium, aluminum, or antimony, as well as aluminum chloride (Bibl.38). In the absence of catalysts, even in the simplest case, on the reaction of two esters of orthosilicic acids, the process proceeds only partially, and equilibrium cannot be attained.
In the presence of a catalyst, magnesium aluminoalcoholate, on heating 4 1/2 hours at the boiling point, the equilibrium state is established, and all the mixed esters are formed in the statistical quantities. The mixing of equimolecular quantities of tetraethoxy- and tetrabutoxysilane leads to the formation of 0.09 mol of tetraethoxysilane, 0.42 mol of triethoxybutoxysilane, 0.66 mol of diethoxybutoxysilane, 0.42 mol of ethoxytributoxysilane, and 0.08 mol of tetrabutoxysilane. When equimolecular quantities of tetraethoxysilane and tetraallyloxysilane react, a mixture is obtained which contains 0.094 mol of tetraethoxysilane, 0.462 mol of triethoxyallyloxysilane, 0.684 mol of diethoxyallyloxysilane, 0.428 mol of ethoxydi allyloxysilane, and 0.074 mol of tetraallyloxysilane.

The reaction of reesterification with esters of the carboxylic acids is performed in a flask which serves at the same time as the retort for a rectification column, with distillation of the volatile products of reaction (Bibl.37). The reaction of tetraethoxysilane with butyl acetate in the presence of aluminum ethylate proceeds according to the formula:

\[ \text{Si(OCH}_2\text{CH}_3)_4 + 4\text{CH}_2\text{COOCH}_3\text{H}_2 \rightarrow \text{Si(OCH}_2\text{CH}_3)_4 + 4\text{CH}_2\text{COOCH}_3\text{H}_2 \]

and 99% of the theoretical quantity of ethyl acetate is distilled off. With vinyl acetate the analogous reaction proceeds quantitatively, but the tetravinylsiloxane formed during the reaction polymerizes during the process of synthesis.

One of the substantial conditions for the completion of the process is the volatility of the organic ester and its continuous removal by way of rectification. In this connection, the reaction of reesterification proceeds most easily of all between tetraethoxysilane or tetramethoxysilane and esters of formic or acetic acid. The higher tetraalkoxysilanes, as well as the esters of the higher carboxylic acids,
reacts with great difficulty.

Esters of inorganic acids, for instance boric acid, enter into the reesterification reaction like the esters of the carboxylic acids:

\[ 3\text{Si(OCH}_3\text{)}_4 + 4\text{B(OC}_4\text{H}_4\text{)}_3 = 3\text{Si(OC}_4\text{H}_5\text{)}_4 + 4\text{B(OCH}_3\text{)}_3 \]

This reaction proceeds with a 96% yield in the presence of magnesium aluminoethylate (Bibl.38), and is of interest as a method of preparing methyl borate, whose synthesis by other methods is considerably more complicated. We may note here that the esters of boric acid may also be prepared by the reaction between esters of orthosilicic acid and boric anhydride.

Other Methods of Preparing Esters

A process which has recently been described (Bibl.28) of esterification of the free hydroxyl groups of the polymeric silicic acid obtained by acidifying a solution of sodium silicate, is of great theoretical interest:

\[ \text{O} - \text{Si(OH)}_2 \cdot \text{C}_4\text{H}_5\text{OH} = \text{O} - \text{Si(OC}_4\text{H}_5\text{)}_2 + \text{H}_2\text{O} \]

As a result of this reaction, a soluble polysiloxane containing an average of 0.613 butoxyl groups to the silicon atom is obtained.

Preparation of polysilicic acid. A solution of 770 g of sodium silicate \((28.4\% \text{SiO}_2; \frac{\text{SiO}_2}{\text{Na}_2\text{O}} = 3.25)\) in 1138 g of water is poured with vigorous stirring into 1710 ml of 7.35% sulfuric acids at 20°C. The solution of sodium silicate is introduced under the layer of sulfuric acid through a tube not more than 2.5 mm in diameter, for 5 min. The acidity of the mixture at the end of the addition of the silicate is 1.7 - 0.5 mg KOH. In order to extract the polymeric silicic acid liberated, 1070 g of tert-butyl alcohol is introduced into the mixture, which is stirred for 15 minutes and then allowed to stand for 16 - 18 hours. The water is then
removed by salting out, by adding 1017 g of sodium chloride to the mixture. The alcohol layer (1540 ml) contains polymeric silicic acid (14% of SiO$_2$), 10 - 15% of water and 0.96% of sodium chloride. The yield of silicic acid is 80 - 85% of theoretical. The preparation is unstable on standing; its molecular weight increases at a rate depending on the concentration, the acidity of the medium, and the temperature.

Esterification. To the solution of polysilicic acid so obtained, an equal volume of normal butyl alcohol, and 6 g of barium chloride to precipitate the traces of sulfuric acid, are added, the mixture is placed in the tank of a rectification column, where, under reduced pressure, the processes of esterification of the free hydroxyl groups of the polymeric silicic acid and of distilling off the water formed during the reaction is performed. To avoid condensation of the free hydroxyl groups and increase the molecular weight of the polymer, the process is commenced at a temperature (in the tank) of 28 - 29%, and a residual pressure of 30 mm. During the course of 2 hours, 1131 ml of distillate is taken off, and the volume is held constant in the tank of the column by adding fresh n-butyl alcohol. When 2 hours have elapsed, the pressure in the tank rises to 60 mm. During the next 5 hours 3260 g of distillate are taken off and 1696 g of n-butyl alcohol is added to the tank. The temperature in the tank is gradually brought up to 60°C.

The reaction mixture now is removed from the tank of the column, purified by adsorbents, filtered, and rectified on a column (reflux ratio 4 : 1) and during the course of 5 hours 485 g of butyl alcohol is introduced into the tank of the column while 752 ml of condensate is distilled from the tank. The temperature in the tank at the end of the rectification reaches 121°C.

The reaction product is repeatedly purified by adsorbents and is diluted with butanol until the SiO$_2$ content of the mixture reaches 20%. 100 ml of the mixture contains 0.11 g of water, 0.03 g of chlorine; the pH of the mixture is 3.8. The amount of solid residue is 33.98%. The residue contains 5% of SiO$_2$ and 28.2% of
carbon, which makes an average of 0.613 Butoxy group to a silicon atom. Measurements of the viscosity of the solutions give grounds for postulating that the molecules of the polymer are of spherical form.

The esterification of polymeric orthosilicic acid by propyl or isopropyl alcohol can be carried out by a similar method (Bibl.39).

Under the action of alcohol on elementary silicon in the presence of catalysts at temperatures of 220°C, a complex mixture is formed, consisting of esters of orthosilicic acid and other products. This reaction has been investigated (Bibl.40) with the object of elucidating the possibility of synthesizing polysiloxanes.

The process is conducted by passing the vapors of the alcohol through tablets of a copper-silicon contact mass obtained by pressing and sintering a mixture of silicon and copper (20%) powders in a current of hydrogen at 1050°C. Only methanol reacts rather actively, and the principal product of the reaction is not polymethylsiloxane, but tetramethoxysilane. The reaction mainly takes the following course:

$$Si + 4\text{CH}_3\text{OH} = \text{Si}(\text{OCCH}_3)_4 + 2\text{H}_2$$

On heating to 300°C, the yield of tetramethoxysilane is 48%, at a temperature of 250°C the yield of the product is 53% of theoretical. The hydrogen formed during the reaction is in part added to the silicon with the formation of a certain quantity of compounds containing the -Si-H bond, and in part is evolved in molecular form, while still another part is used in the reduction of methanol:

$$\text{CH}_3\text{OH} + 2\text{H} = \text{CH}_4 + \text{H}_2\text{O}$$

Methane is a byproduct of the reaction. It is collected in a receiver which is cooled by liquid air. Water hydrolyzes the ester formed, so that a certain part of the reaction product consists of polymethoxysiloxanes.

Ethanol reacts with a mixture of silicon and copper powders under similar
conditions, forming 10% of polyethoxysiloxanes together with traces of compounds containing the \(-\text{Si-O-}\) bond (Bibl.39).

By careful analysis of the intermediate fractions and their hydrolyzates, the presence of an insignificant quantity of compounds containing the \(-\text{Si-C}\) bond in the reaction products has been established, but it was not possible to isolate the individual methylsiloxanes or methylethoxysilanes. The search for process catalysts other than those ordinarily used in the direct synthesis of alkylchlorosilane was unsuccessful.

The conduct of the reaction between the alcohols and the contact mass in a state of suspension has been proposed (Bibl.41).

A synthesis of esters of orthosilicic acid by the reaction of alcohols with metallic silicides has been described (Bibl.42). Thus, under the action of methanol on magnesium silicide, the following reaction takes place:

$$\text{Mg}_2\text{Si} + 8\text{CH}_3\text{OH} = \text{Si}(\text{OCH}_3)_4 + 2\text{Mg}(\text{OCH}_3)_2 + 4\text{H}_2$$

In a flask 1500 ml of methanol are placed, and, under cooling and stirring, 130 g of magnesium silicide is added over a period of 2 hours. The mixture is gradually warmed until the evolution of hydrogen stops (total quantity evolved, 36 liters), and the tetramethoxysilane (110 g) is then distilled off under atmospheric pressure.

The preparation of esters of orthosilicic acid by way of silicon disulfide, which is easily synthesized from the elements, is of considerable interest (Bibl.19):

$$\text{Si} + 2\text{S} = \text{S}_{2}\text{S}_2$$
$$\text{S}_2\text{S}_2 + 4\text{ROH} = \text{Si}(\text{OR})_4 + 2\text{H}_2\text{S}$$

From 2 kg of methanol and 1150 g of 80% silicon disulfide, 1390 g of tetramethoxy-silane is obtained. When the methanol is replaced by the same amount of ethanol,
1800 g of tetraethoxysilane is obtained. A substantial advantage of the process is the absence of the side reactions that occur on the esterification of SiCl$_4$ owing to the liberation of HCl. Various phenols may be used for the esterification of silicon disulfide. The reaction with o,o-dichlorophenol gave tetra-(o,o-dichlorophenoxy)-silane, Si(OC$_6$H$_3$Cl$_2$)$_4$.

In the reaction between silicon disulfide and an aqueous alcohol, polyalkoxy-siloxanes are formed. In the reaction with insufficient alcohol, polymeric compounds are formed, containing -Si-S-Si- bonds of the type:

$$(RO)_2Si[(RO)Si]_xSi(OR)_2$$

No formation of compounds containing the group -Si-S-R has been noted.

In connection with the fact that silicon disulfide is less active than SiCl$_4$, the reaction of SiS$_2$ with organic acids is a more convenient method of preparing mixed anhydrides of orthosilicic acid.

$$SiS_2 + 4HOOCR = Si(OCOR)_4 + 2H_2S$$

By this reaction a number of mixed anhydrides of orthosilicic acid were obtained - Si(OCOR)$_4$ where R = CH$_3$, C$_6$H$_5$, CH$_2$Cl, C$_{17}$H$_{35}$.

**Industrial Production of Esters of Orthosilicic Acid**

On the industrial scale, the esters of orthosilicic acid are prepared, either for immediate use (Bibl.43) (manufacture of coatings, impregnating materials, molds for precision casting (Bibl.44), cements, special types of gels, etc.), or for the synthesis of the substituted esters of orthosilicic acid (Bibl.45).

The reaction between SiCl$_4$ and alcohol is exclusively used for the preparation of esters of orthosilicic acid on an industrial scale. The process is conducted in continuous run apparatus, or (more often), in batch apparatus, by pouring SiCl$_4$ into the alcohol (or vice versa), under stirring, followed by heating (Bibl.45). The most important and most widely used process is the esterification of silicon
tetrachloride by ethanol, since the ethyl ester of orthosilicic acid, either in the pure form or hydrolyzed, has come to be most widely used in technology, owing to its cheapness, the relative simplicity of its preparation, and the fact that it is less toxic than tetramethoxysilane. The industrial product is put out in varying degrees of purity, (depending on the uses to which it is to be put).

In Great Britain (Bibl.44), the esterification of silicon tetrachloride is conducted by the action of technical ethyl alcohol (specific gravity 0.822); as a result of the reaction, the so-called "ethyl silicate 40", is obtained. This is a partially hydrolyzed product containing about 40% of SiO₂ (specific gravity 1.05-1.07). The high SiO₂ content in "ethyl silicate 40" encourages its use in the manufacture of coatings and cements.

In the United States (Bibl.43, 45), the manufacture of "ethyl silicate 40" has commenced only in recent years. Before that, pure and "condensed ethyl silicate" were produced. This latter is a product obtained by esterification of silicon tetrachloride by 99% ethyl alcohol, followed by the distillation of the excess alcohol at a temperature running up to 110°C. For the synthesis of the substituted esters of orthosilicic acid, "pure" (distilled) ester, is manufactured, containing 90% of the fraction boiling at 160 - 170°C and having an acidity not over 0.05%. The price of such a product is considerably higher than the price of the technical product, and the SiO₂ content in it does not exceed 28%, so that it is not economic to use the pure tetraethoxysilane in making coatings or cement composition.

Physical Properties

The esters of orthosilicic acid with aliphatic alcohols are colorless transparent liquids; the esters of orthosilicic acid with phenols, as a rule, are crystalline products. The purification of the esters of orthosilicic acid from traces of alcohol or haloesters involves certain difficulties, so that the tetraalkoxysilanes are usually produced in the form of thick liquids which crystallize only on strong cooling. All the esters of orthosilicic acid, in the absence of moisture, are
stable substances that can be distilled without decomposition. The lower esters of orthosilicic acid have a specific odor, while the higher esters have no odor at room temperature; they do not dissolve in water and are slowly hydrolyzed by it, but are readily soluble in organic solvents.

With increasing molecular weight of the compounds, its density decreases and its boiling point rises by about 12°C for each additional CH₂ group.

Tables 22, 23, 24 give the physical properties of alkoxy- and aryloxysilanes. Table 25 gives the properties of the esters of polysiloxanes, and Table 26 the properties of the trialkylsiloxanes.

The boiling points, unless the pressure is given, are given at 760 mm.

**Chemical Properties**

Most of the reactions of the esters of orthosilicic acid are due to the presence of the reactive -Si-O-C- bonds in their molecules. Let us consider the most important and typical reactions of the esters of orthosilicic acid.

**The Reaction of Hydrolysis**

An extremely important property of the esters of orthosilicic acid is their ability to split off the alkoxy group under the action of water:

\[
-\text{Si-OR} + \text{H}_2\text{O} = -\text{Si-OH} + \text{ROH}
\]

The reaction is always accompanied by intermolecular condensation of the hydrolysis products, and by the formation of polysiloxanes. I have investigated the mechanism of hydrolysis and condensation in detail (Bibl. 46, 47) on the example of the ethyl ether of orthosilicic acid, in the course of which investigation I isolated and studied a number of polyethoxysiloxanes of the general formulas \((\text{C}_2\text{H}_5\text{O})\text{Si(OC}_2\text{H}_5\text{)}_2\text{O}_x\text{C}_2\text{H}_5\), where \(x = 2, 4, \text{and} 6\). The results of this work allow the conclusion that
the hydrolysis of these esters proceeds by a pattern common for the reactions of all organosilicon monomers containing readily hydrolyzable groups or atoms bound to the silicon atom.

Let us consider the processes taking place when an aqueous alcohol is gradually

Table 22

Physical Properties of the Aliphatic Esters of Orthosilicic Acid

<table>
<thead>
<tr>
<th>a) Name</th>
<th>b) Formula</th>
<th>c) Boiling Point, °C</th>
<th>d) Specific Gravity, $d_20$</th>
<th>e) Refractive Index, $n_D$</th>
<th>f) Bibliography</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetramethoxysilane</td>
<td>(OC,H)$_4$Si</td>
<td>121-122</td>
<td>1.032</td>
<td>1.3881</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>(759 mm)</td>
<td>27-27</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(12 mm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetraethoxysilane</td>
<td>(OC$_2$H$_5$)$_4$Si</td>
<td>166.5</td>
<td>0.9676 ($6^o$)</td>
<td>1.3837</td>
<td>8, 10</td>
</tr>
<tr>
<td>Tetrapropoxysilane</td>
<td>(OC$_3$H$_7$)$_4$Si</td>
<td>77-80</td>
<td>0.918</td>
<td>1.4015</td>
<td>102</td>
</tr>
<tr>
<td>Tetraisopropoxysilane</td>
<td>(OC$_4$H$_9$)$_4$Si</td>
<td>163 (20 mm)</td>
<td>0.899</td>
<td>1.4128</td>
<td>113</td>
</tr>
<tr>
<td>Tetrabutoxysilane</td>
<td>(OC$<em>5$H$</em>{11}$)$_4$Si</td>
<td>150-152</td>
<td>0.913 ($25^o$)</td>
<td>1.4128</td>
<td>114</td>
</tr>
<tr>
<td>Tetraisobutoxysilane</td>
<td>(OC$<em>6$H$</em>{13}$)$_4$Si</td>
<td>225-260</td>
<td>0.953</td>
<td>1.4131</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>(18 mm)</td>
<td>143-145</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(18 mm)</td>
<td>141-142</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0,3 mm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetraamylxysilane</td>
<td>(C$_3$H$_7$)$_4$Si</td>
<td>322-323</td>
<td>0.953 ($15^o$)</td>
<td>-</td>
<td>16</td>
</tr>
<tr>
<td>Tetraisamylxysilane</td>
<td>([H₃C][H₃C][H₂O]$_4$Si</td>
<td>174-176</td>
<td>0.893</td>
<td>-</td>
<td>10, 16</td>
</tr>
<tr>
<td>Tetrahexoxysilane</td>
<td>(C$<em>6$H$</em>{13}$)$_4$Si</td>
<td>222-234</td>
<td>0.888</td>
<td>-</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>(13 mm)</td>
<td>213.5</td>
<td>0.876</td>
<td>1.4400</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>(4 mm)</td>
<td></td>
<td></td>
<td></td>
<td>116</td>
</tr>
<tr>
<td>Tetrapentylxysilane</td>
<td>(C$<em>7$H$</em>{15}$)$_4$Si</td>
<td>200-215</td>
<td>0.9117 ($36^o$)</td>
<td>-</td>
<td>103</td>
</tr>
<tr>
<td>Tetrapentyloxysilane</td>
<td>(C$<em>7$H$</em>{17}$O)$_4$Si</td>
<td>240</td>
<td></td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(3 mm)</td>
<td></td>
<td></td>
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<td>47</td>
</tr>
<tr>
<td>Tetraphexoxysilane</td>
<td>(C$<em>8$H$</em>{19}$)$_4$Si</td>
<td>134.5-135</td>
<td>0.9842 ($17^o$)</td>
<td>1.4336</td>
<td>12</td>
</tr>
<tr>
<td>Tetraallyloxysilane</td>
<td>(CH$_2$=CHCH$_2$O)$_4$Si</td>
<td>148-148.5</td>
<td></td>
<td>-</td>
<td>27</td>
</tr>
<tr>
<td>Tetramethallyloxethoxysilane</td>
<td>(CH$_3$CH=CHCH$_2$O)$_4$Si</td>
<td>177-180</td>
<td></td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Tetra-2-chloroethoxysilane</td>
<td>(Cl=CH$_2$-CHO)$_4$Si</td>
<td>213-214</td>
<td>1.4610 (14$)$</td>
<td>1.17</td>
<td>117</td>
</tr>
<tr>
<td>Tetra-2,3-dichloroisopropoxysilane</td>
<td>(Cl-CH$_2$-CHO)$_4$Si</td>
<td>153-154</td>
<td></td>
<td>1.4641 (20$^o$)</td>
<td></td>
</tr>
<tr>
<td>Tetra-2-chloroethoxysilane</td>
<td>(Cl=CH$_2$-CHO)$_4$Si</td>
<td>184</td>
<td></td>
<td>1.4641 (20$^o$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(7 mm)</td>
<td>195-200</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>(15 mm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Boiling Point, °C; d) Specific Gravity, $d_20$; e) Refractive Index, $n_D$; f) Bibliography
Table 23
Physical Properties of the Aliphatic and Aromatic Esters of Orthosilicic Acid

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c)</th>
<th>d)</th>
<th>e)</th>
<th>f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetraphenoxysilane</td>
<td>(C₆H₆O)₄Si</td>
<td>260</td>
<td>415-420</td>
<td>280</td>
<td>90.91</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>47-48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetra-m-cresoxysilane</td>
<td>(CH₃C₆H₄O)₄Si</td>
<td>443-445</td>
<td></td>
<td></td>
<td>118</td>
</tr>
<tr>
<td>Tetra-p-cresoxysilane</td>
<td>(CH₃C₆H₄O)₄Si</td>
<td>442-445</td>
<td>69-70</td>
<td></td>
<td>118</td>
</tr>
<tr>
<td>Tetra-o-xyleneoxy-</td>
<td>[(CH₃)C₆H₄O]₄Si</td>
<td>450</td>
<td></td>
<td></td>
<td>105.5</td>
</tr>
<tr>
<td>silane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetra-m-xyleneoxy-</td>
<td>[C(CH₃)C₆H₄O]₄Si</td>
<td>380</td>
<td></td>
<td></td>
<td>105</td>
</tr>
<tr>
<td>silane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetra-isobutylphenoxysilane</td>
<td>[(CH₃)CH₂C₆H₄O]₄Si</td>
<td>380</td>
<td></td>
<td></td>
<td>105</td>
</tr>
<tr>
<td>Tetra-isomethylphenoxysilane</td>
<td>[(CH₃)CH₂C₆H₄O]₄Si</td>
<td>380</td>
<td></td>
<td></td>
<td>105</td>
</tr>
<tr>
<td>Tetra-thymoloxysilane</td>
<td>[(CH₃)CH₂C₆H₄O]₄Si</td>
<td>380</td>
<td></td>
<td></td>
<td>105</td>
</tr>
<tr>
<td>Tetra-carvacrolosilane</td>
<td>[(CH₃)CH₂C₆H₄O]₄Si</td>
<td>380</td>
<td></td>
<td></td>
<td>105</td>
</tr>
<tr>
<td>Tetra-benzyloxysilane</td>
<td>[(CH₃)C₆H₄O]₄Si</td>
<td>380</td>
<td></td>
<td></td>
<td>105</td>
</tr>
<tr>
<td>Tetra-isooctylsilane</td>
<td>(CH₃)C₆H₄O]₄Si</td>
<td>380</td>
<td></td>
<td></td>
<td>105</td>
</tr>
<tr>
<td>Tetra-thymoloxysilane</td>
<td>[(CH₃)CH₂C₆H₄O]₄Si</td>
<td>380</td>
<td></td>
<td></td>
<td>105</td>
</tr>
<tr>
<td>Tetra-p-bromophenoxysilane</td>
<td>[(CH₃)C₆H₄O]₄Si</td>
<td>380</td>
<td></td>
<td></td>
<td>105</td>
</tr>
<tr>
<td>Hexamethoxy-m-</td>
<td>(BrC₆H₄O)₄Si</td>
<td>354</td>
<td></td>
<td></td>
<td>93.117</td>
</tr>
<tr>
<td>dioxophenylene-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>disilane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hexamethoxy-p-</td>
<td>[(CH₃O)₂SiO]C₆H₄</td>
<td>net distil.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dioxophenylene-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>disilane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetra-(cis-9-benzeneoctadecene-1-oxo)-silane</td>
<td>[(CH₃O)₂SiO]C₆H₄</td>
<td>450</td>
<td></td>
<td></td>
<td>105</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
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<td></td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Boiling Point, °C; d) Melting Point, °C;
e) Refractive Index; f) Bibliography
### Table 24

**Physical Properties of Mixed Esters of Orthosilicic Acid**

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c)</th>
<th>d)</th>
<th>e)</th>
<th>f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trimethoxysilane</td>
<td>(CH₃O)₂Si(OCH₃)₂</td>
<td>133-135</td>
<td>1,023</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td>Dimethoxysilane</td>
<td>(CH₃O)₂Si(OCH₃)₂</td>
<td>143-146</td>
<td>1,004</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td>Methoxytritylsilane</td>
<td>(CH₃O)₃Si(OCH₃)₂</td>
<td>155-157</td>
<td>0,989</td>
<td>2,27</td>
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</tr>
<tr>
<td>Triethoxysilyl</td>
<td>(CH₃O)₂Si(OCH₃)₂</td>
<td>70,5</td>
<td>1,3919</td>
<td>12,27</td>
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</tr>
<tr>
<td>Ethoxysilyl</td>
<td>(CH₃O)₂Si(OCH₃)₂</td>
<td>95</td>
<td>1,4110</td>
<td>12,27</td>
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</tr>
<tr>
<td>Methoxytritylsilane</td>
<td>(CH₃O)₃Si(OCH₃)₂</td>
<td>116</td>
<td>1,4252</td>
<td>47</td>
<td></td>
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<tr>
<td>Triethoxysilyl</td>
<td>(CH₃O)₂Si(OCH₃)₂</td>
<td>83,5</td>
<td>1,4003</td>
<td>12,27</td>
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<tr>
<td>Ethoxysilyl</td>
<td>(CH₃O)₂Si(OCH₃)₂</td>
<td>115</td>
<td>1,4156</td>
<td>12,27</td>
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<tr>
<td>Methoxytritylsilane</td>
<td>(CH₃O)₃Si(OCH₃)₂</td>
<td>128</td>
<td>1,4320</td>
<td>12,27</td>
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<tr>
<td>Triethoxysilyl</td>
<td>(CH₃O)₂Si(OCH₃)₂</td>
<td>2255-235</td>
<td>--</td>
<td>72</td>
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<tr>
<td>Ethoxysilyl</td>
<td>(CH₃O)₂Si(OCH₃)₂</td>
<td>215-220</td>
<td>1,3973</td>
<td>12,27</td>
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<tr>
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<td>(CH₃O)₃Si(OCH₃)₂</td>
<td>93,5-94</td>
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<tr>
<td>Triethoxysilyl</td>
<td>(CH₃O)₂Si(OCH₃)₂</td>
<td>108</td>
<td>1,4098</td>
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<td>1,4230</td>
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<td>93</td>
<td>1,4051</td>
<td>12,27</td>
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<td>116</td>
<td>1,4200</td>
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<td>Ethoxysilyl</td>
<td>(CH₃O)₂Si(OCH₃)₂</td>
<td>133</td>
<td>1,4320</td>
<td>12,27</td>
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<td>78</td>
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<tr>
<td>Methoxytritylsilane</td>
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<td>12,27</td>
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<tr>
<td>Triethoxysilyl</td>
<td>(CH₃O)₂Si(OCH₃)₂</td>
<td>144-146</td>
<td>1,4112</td>
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<td>99-100</td>
<td>1,369</td>
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<td>Triethoxysilyl</td>
<td>(CH₃O)₂Si(OCH₃)₂</td>
<td>99-100</td>
<td>1,369</td>
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<td>85,5-86,5</td>
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<tr>
<td>Methoxytritylsilane</td>
<td>(CH₃O)₃Si(OCH₃)₂</td>
<td>216-228</td>
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<tr>
<td>Triethoxysilyl</td>
<td>(CH₃O)₂Si(OCH₃)₂</td>
<td>125-130</td>
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<tr>
<td>Ethoxysilyl</td>
<td>(CH₃O)₂Si(OCH₃)₂</td>
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<td>Methoxytritylsilane</td>
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<td>290-285</td>
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a) Name; b) Formula; c) Boiling Point, °C; d) Refractive Index, n₂⁰; e) Specific Gravity, d₄⁰; f) Bibliography
| a) Name; b) Formula; c) Boiling Point, °C; d) Refractive Index, nD; |
|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| liethoxydiphenoxydilute silane   | \((\text{C}_4\text{H}_7\text{O})_2\text{Si(OCH}_3\text{H}_3\text{)}_2\) | 302–304                         | 47                             |
| (CH\textsubscript{2}–CH\textsubscript{2}O\textsubscript{2})\textsubscript{5}Si(OCH\textsubscript{3}H\textsubscript{3})     | 197–198                         |                                 |
| 4.5–5.0 (50 mm)                | 1.4204                          | 27                             |
| Triaallycloxypropyne silane     | \((\text{CH}_3–\text{CH}–\text{CH}–\text{CH}_3)\text{Si(OCH}_3\text{H}_3\text{)}_2\) | 57–58                           | 27                             |
| (CH\textsubscript{2}–CH\textsubscript{2}O\textsubscript{2})\textsubscript{5}Si(OCH\textsubscript{3}H\textsubscript{3})     | 2 (mm)                          |                                 |
| Triaallycloxydiene silane       | \((\text{CH}_3–\text{CH}–\text{CH}–\text{CH}_3)\text{Si(OCH}_3\text{H}_3\text{)}_2\) | 74.5–75.0                       | 27                             |
| (CH\textsubscript{2}–CH\textsubscript{2}O\textsubscript{2})\textsubscript{5}Si(OCH\textsubscript{3}H\textsubscript{3})     | 2 (mm)                          |                                 |
| Triaallycloxybutyne silane      | \((\text{CH}_3–\text{CH}–\text{CH}–\text{CH}_3)\text{Si(OCH}_3\text{H}_3\text{)}_2\) | 85.5–86.5                       | 27                             |
| (CH\textsubscript{2}–CH\textsubscript{2}O\textsubscript{2})\textsubscript{5}Si(OCH\textsubscript{3}H\textsubscript{3})     | 3 (mm)                          |                                 |
| Triaallycloxyisobutoxy silane   | \((\text{CH}_3–\text{CH}–\text{CH}–\text{CH}_3)\text{Si(OCH}_3\text{H}_3\text{)}_2\) | 91.0–91.5                       | 27                             |
| (CH\textsubscript{2}–CH\textsubscript{2}O\textsubscript{2})\textsubscript{5}Si(OCH\textsubscript{3}H\textsubscript{3})     | 3 (mm)                          |                                 |
| Triaallycloxydiisobutoxy silane | \((\text{CH}_3–\text{CH}–\text{CH}–\text{CH}_3)\text{Si(OCH}_3\text{H}_3\text{)}_2\) | 73.0–73.5                       | 27                             |
| (CH\textsubscript{2}–CH\textsubscript{2}O\textsubscript{2})\textsubscript{5}Si(OCH\textsubscript{3}H\textsubscript{3})     | 2 (mm)                          |                                 |
| Triaallycloxy-tertisobutoxy silane | \((\text{CH}_3–\text{CH}–\text{CH}–\text{CH}_3)\text{Si(OCH}_3\text{H}_3\text{)}_2\) | 61.5–62.0                       | 27                             |
| (CH\textsubscript{2}–CH\textsubscript{2}O\textsubscript{2})\textsubscript{5}Si(OCH\textsubscript{3}H\textsubscript{3})     | 2 (mm)                          |                                 |
| Triaallycloxy-tertisobutoxy silane | \((\text{CH}_3–\text{CH}–\text{CH}–\text{CH}_3)\text{Si(OCH}_3\text{H}_3\text{)}_2\) | 104.5–105.5                     | 28                             |
| (CH\textsubscript{2}–CH\textsubscript{2}O\textsubscript{2})\textsubscript{5}Si(OCH\textsubscript{3}H\textsubscript{3})     | 3 (mm)                          |                                 |
| Triaallycloxy-α-naphthiloxy silane | \((\text{CH}_3–\text{CH}–\text{CH}–\text{CH}_3)\text{Si(OCH}_3\text{H}_3\text{)}_2\) | 128.5–129.0                     | 28                             |
| (CH\textsubscript{2}–CH\textsubscript{2}O\textsubscript{2})\textsubscript{5}Si(OCH\textsubscript{3}H\textsubscript{3})     | 3 (mm)                          |                                 |
| Triaallycloxy-α-naphthiloxy silane | \((\text{CH}_3–\text{CH}–\text{CH}–\text{CH}_3)\text{Si(OCH}_3\text{H}_3\text{)}_2\) | 225–228,0                       | 27                             |
| (CH\textsubscript{2}–CH\textsubscript{2}O\textsubscript{2})\textsubscript{5}Si(OCH\textsubscript{3}H\textsubscript{3})     | 3 (mm)                          |                                 |
| Triallycloxyethylcloxy silane   | \((\text{CH}_3–\text{CH}–\text{CH}–\text{CH}_3)\text{Si(OCH}_3\text{H}_3\text{)}_2\) | 117–118                         | 1.1306                         |
| (CH\textsubscript{2}–CH\textsubscript{2}O\textsubscript{2})\textsubscript{5}Si(OCH\textsubscript{3}H\textsubscript{3})     | 3 (mm)                          |                                 |
| Trimethylallycloxyisobutoxy silane | \((\text{CH}_3–\text{CH}–\text{CH}–\text{CH}_3)\text{Si(OCH}_3\text{H}_3\text{)}_2\) | 1.14–115                        | 1.4216                         |
| (CH\textsubscript{2}–CH\textsubscript{2}O\textsubscript{2})\textsubscript{5}Si(OCH\textsubscript{3}H\textsubscript{3})     | 3 (mm)                          |                                 |
| Trimethylallycloxyisobutoxy silane | \((\text{CH}_3–\text{CH}–\text{CH}–\text{CH}_3)\text{Si(OCH}_3\text{H}_3\text{)}_2\) | 106.5–107.5                     | 1.4135                         |
| (CH\textsubscript{2}–CH\textsubscript{2}O\textsubscript{2})\textsubscript{5}Si(OCH\textsubscript{3}H\textsubscript{3})     | 3 (mm)                          |                                 |
| Trimethylallycloxyisobutoxy silane | \((\text{CH}_3–\text{CH}–\text{CH}–\text{CH}_3)\text{Si(OCH}_3\text{H}_3\text{)}_2\) | 82.0–83.0                       | 1.4219                         |
| (CH\textsubscript{2}–CH\textsubscript{2}O\textsubscript{2})\textsubscript{5}Si(OCH\textsubscript{3}H\textsubscript{3})     | (2 mm)                          |                                 |
| Triaallycloxy-tertisobutoxy silane | \((\text{CH}_3–\text{CH}–\text{CH}–\text{CH}_3)\text{Si(OCH}_3\text{H}_3\text{)}_2\) | 150                             | 28                             |
| (CH\textsubscript{2}–CH\textsubscript{2}O\textsubscript{2})\textsubscript{5}Si(OCH\textsubscript{3}H\textsubscript{3})     | (20 mm)                         |                                 |
| Triethoxymacetyl silane         | \((\text{CH}_3–\text{CH}–\text{CH}–\text{CH}_3)\text{Si(OCH}_3\text{H}_3\text{)}_2\) | 235–240                         | 28                             |
| (CH\textsubscript{2}–CH\textsubscript{2}O\textsubscript{2})\textsubscript{5}Si(OCH\textsubscript{3}H\textsubscript{3})     | (24 mm)                         |                                 |
| Tripropoxymacetyl silane        | \((\text{CH}_3–\text{CH}–\text{CH}–\text{CH}_3)\text{Si(OCH}_3\text{H}_3\text{)}_2\) | 104–105                         | 107                            |
| (CH\textsubscript{2}–CH\textsubscript{2}O\textsubscript{2})\textsubscript{5}Si(OCH\textsubscript{3}H\textsubscript{3})     | (24 mm)                         |                                 |
| Isopropoxymacetyl silane        | \((\text{CH}_3–\text{CH}–\text{CH}–\text{CH}_3)\text{Si(OCH}_3\text{H}_3\text{)}_2\) | not distillable                 | 28                             |
| (CH\textsubscript{2}–CH\textsubscript{2}O\textsubscript{2})\textsubscript{5}Si(OCH\textsubscript{3}H\textsubscript{3})     |                                 |                                 |
| Vethoxy- (ethoxy)-phenoxypenta-tertisobutoxy silane | \((\text{CH}_3–\text{CH}–\text{CH}–\text{CH}_3)\text{Si(OCH}_3\text{H}_3\text{)}_2\) | net distillable                 | 28                             |
| (CH\textsubscript{2}–CH\textsubscript{2}O\textsubscript{2})\textsubscript{5}Si(OCH\textsubscript{3}H\textsubscript{3})     |                                 |                                 |

Hydrolysis of Tetraethoxysilane in a Water-Alcohol Medium

The addition of the first drops of aqueous alcohol to tetraethoxysilane results in processes which are represented rather accurately by the following equations:

poured into tetraethoxysilane.

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<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c)</th>
<th>d)</th>
<th>e)</th>
<th>f)</th>
<th>g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetracmethoxypentasiloxane</td>
<td>O₃Si₄(OCH₃)₁₂</td>
<td>207–215</td>
<td>1.222</td>
<td>0.116</td>
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<tr>
<td>Tetraecmethoxyhexasiloxane</td>
<td>O₃Si₄(OCH₃)₁₄</td>
<td>230–250</td>
<td>1.230</td>
<td>0.170</td>
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<td>Octadecamethoxynonasiloxane</td>
<td>O₃Si₄(OCH₃)₁₈</td>
<td>190–205</td>
<td>1.256</td>
<td>0.318</td>
<td>110</td>
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<tr>
<td>Dodecamethoxydecasiloxane</td>
<td>O₃Si₄(OCH₃)₂₀</td>
<td>220–240</td>
<td>1.260</td>
<td>0.375</td>
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<td>Tetrapethoxydisiloxane</td>
<td>O₃Si₂[OC₃H₅]₂</td>
<td>94–97</td>
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<td>21.24</td>
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<td>Hexaethoxydisiloxane</td>
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<td>Octaethoxytrisiloxane</td>
<td>O₃Si₄(OCH₃)₄</td>
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<td>Octaethoxycyclotetrasiloxane</td>
<td>O₃Si₄(OC₃H₅)₄</td>
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<td>1.071</td>
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<td>O₃Si₂(OC₃H₅)₆</td>
<td>208–212</td>
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<tr>
<td>Tetradecamethoxynonasiloxane</td>
<td>O₃Si₄(OCH₃)₂₀</td>
<td>242–247</td>
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<td>—</td>
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<tr>
<td>Tetrapethoxyhexasiloxane</td>
<td>O₃Si₁₂[OC₃H₅]₂</td>
<td>205–220</td>
<td>—</td>
<td>—</td>
<td>110</td>
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<tr>
<td>Hexpropoxydisiloxane</td>
<td>O₃Si[OC₃H₅CH=CH₂]₆</td>
<td>160–161</td>
<td>1.1394</td>
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<tr>
<td>Hexaallyloxydisiloxane</td>
<td>O₃Si[OC₃H₅CH=CH₂]₆</td>
<td>176–178</td>
<td>1.4414</td>
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<td>Hexamethylallyldisiloxane</td>
<td>O₃Si[OC₃H₅CH=CH₂]₆</td>
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<td>—</td>
<td>49.120</td>
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<td>Hexabutoxynysiloxane</td>
<td>O₃Si[OC₃H₅CH=CH₂]₆</td>
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<td>1.4220</td>
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<td>Hexabutoxycyclooctasiloxane</td>
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<td>Octabutoxycyclotetrasiloxane</td>
<td>O₃Si[OC₃H₅CH=CH₂]₆</td>
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<td>—</td>
<td>49.120</td>
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<td>Decabutoxycyclononasiloxane</td>
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<td>271–280</td>
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<td>Dodecaboxyhexasiloxane</td>
<td>O₃Si[OC₃H₅CH=CH₂]₆</td>
<td>300–320</td>
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<td>49.120</td>
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<td>Hexadecaboxyoctasiloxane</td>
<td>O₃Si[OC₃H₅CH=CH₂]₆</td>
<td>192–194</td>
<td>—</td>
<td>—</td>
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<tr>
<td>Hexaphenoxydisiloxane</td>
<td>O₃Si[OC₃H₅CH=CH₂]₆</td>
<td>200–204</td>
<td>—</td>
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<tr>
<td>Hexaphenoxydisiloxane</td>
<td>O₃Si[OC₃H₅CH=CH₂]₆</td>
<td>200–204</td>
<td>—</td>
<td>—</td>
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<tr>
<td>Hexacyclohexyldisiloxane</td>
<td>O₃Si[OC₃H₅CH=CH₂]₆</td>
<td>149–151</td>
<td>1.1080</td>
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<tr>
<td>Hexacyclodecylhexyldisiloxane</td>
<td>O₃Si[OC₃H₅CH=CH₂]₆</td>
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<td>1.1080</td>
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<tr>
<td>Tetraallyldiethoxydisiloxane</td>
<td>O₃Si[OC₃H₅CH=CH₂]₆</td>
<td>250–260</td>
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<tr>
<td>Tetraethoxydibenzyl</td>
<td>O₃Si[OC₃H₅CH=CH₂]₆</td>
<td>149–151</td>
<td>1.1080</td>
<td>—</td>
<td>4</td>
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</table>

a) Name; b) Formula; c) Boiling Point, °C; d) Specific Gravity, d⁴₀; e) Refractive Index, nD⁴₀; f) Absolute Viscosity, Poises; g) Bibliography
<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c)</th>
<th>d)</th>
<th>e)</th>
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<tbody>
<tr>
<td>Hexamethoxydisiloxane</td>
<td>OSi(OC(2H5)3)2</td>
<td>195-205</td>
<td>1.122</td>
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<td>Octamethoxytrisiloxane</td>
<td>O2Si(OC(2H5)3)3</td>
<td>248-258</td>
<td>1.163</td>
<td>0.038</td>
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<tr>
<td>Decamethoxytetrasiloxane</td>
<td>O3Si(OC(2H5)3)4</td>
<td>170-195</td>
<td>1.197</td>
<td>0.074</td>
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</tbody>
</table>

* $n^20_D = 1.3850$

** $n^20_D = 1.40759$

a) Name; b) Formula; c) Boiling Point, °C; d) Specific Gravity, $d^20_4$; e) Refractive Index, $n^20_D$; f) Absolute Viscosity, Poises; g) Bibliography

\[
\begin{align*}
\text{Si(OC(2H5)3)4} + H_2O &\rightarrow (\text{C}_8\text{H}_{16}O)_3\text{SiOH} + \text{C}_8\text{H}_{17}OH \\
2(\text{C}_8\text{H}_{16}O)_3\text{SiOH} &\rightarrow (\text{C}_8\text{H}_{16}O)_5\text{SiOSiOC(2H5)3} + H_2O \\
(\text{C}_8\text{H}_{16}O)_5\text{SiOSiOC(2H5)3} + H_2O &\rightarrow (\text{C}_8\text{H}_{16}O)_7\text{SiOSiOC(2H5)5}OH + \text{C}_8\text{H}_{17}OH \\
(\text{C}_8\text{H}_{16}O)_7\text{SiOSiOC(2H5)5}OH + 11\text{HOSiOC(2H5)3} &\rightarrow \\
&\rightarrow (\text{C}_8\text{H}_{16}O)[\text{SiOC(2H5)4}]_3\text{C}_8\text{H}_{17} + H_2O \text{ etc.}
\end{align*}
\]

The condensation of the intermediate products of hydrolysis, the alkoxyhydroxy-silanes so formed, proceeds, apparently, almost immediately after the hydrolysis, since up to now it has not been possible to isolate in the pure state any individual alkoxyhydroxysilane of low molecular weight, for instance $\text{(C}_2\text{H}_5\text{O})_3\text{SiOH}$. When an insignificant quantity of water is introduced, linear polymers are for the most part formed; thus, for example, when 0.5 mol of water per mol of tetraethoxysilane is introduced into the reaction, I have obtained hexamethoxydisiloxane as the principal reaction product (Bibl. 46, 47); when 0.75 mol of water is used, decaethoxytetrasiloxane; and when 0.82 mol of water is used, tetradecaethoxyhexasiloxane (Cf. Table 27). Later on, the hydrolysis of the side alkoxy groups, with the formation of branched molecules, probably also takes place (in the individual form such products
### Table 26

**Physical Properties of Trialkylsiloxanes**

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c) °C</th>
<th>d) $d_4^{25}$</th>
<th>e) $n_D^{1^o}$</th>
<th>f)</th>
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<tbody>
<tr>
<td>Triethoxysilane</td>
<td>HSi(OCH$_3$)$_3$</td>
<td>132–135</td>
<td>0.8745</td>
<td>108.121</td>
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<tr>
<td>Triallyloxsilane</td>
<td>HSi(CH=CH$_2$)$_3$</td>
<td>110–112 (14 mm)</td>
<td>0.9836</td>
<td>1.4284</td>
<td>0.00</td>
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<tr>
<td>Tripropoxysilane</td>
<td>HSi(OC$_3$H$_7$)$_3$</td>
<td>190–194 (750 mm)</td>
<td>0.882</td>
<td>1.427</td>
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<tr>
<td>Triisopropoxysilane</td>
<td>HSi(OCH(CHOH)$_2$CH$_2$)$_3$</td>
<td>101–102 (750 mm)</td>
<td>0.985 (19.7°)</td>
<td>120</td>
<td></td>
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<tr>
<td>Tributoxysilane</td>
<td>HSi(OCH(CH$_3$)$_2$)$_3$</td>
<td>190–194 (750 mm)</td>
<td>0.882</td>
<td>109</td>
<td></td>
</tr>
<tr>
<td>Tri-sec-butoxysilane</td>
<td>HSi(OCH(CHOH)$_3$CH$_2$)$_3$</td>
<td>213–215 (13 mm)</td>
<td>0.8861</td>
<td>1.4054</td>
<td>108,121</td>
</tr>
<tr>
<td>Triallyloxysilane</td>
<td>HSi(OCH(CHOH)$_3$CH$_2$)$_3$</td>
<td>132–135 (5 mm)</td>
<td>0.8710 (27°)</td>
<td>1.4210</td>
<td>120</td>
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<td>Triisamyloxysilane</td>
<td>HSi(OCH(CHOH)$_3$CH$_2$)$_3$</td>
<td>301–305</td>
<td>0.985 (15°)</td>
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<tr>
<td>Trihexylloxysilane</td>
<td>HSi(OCH(CHOH)$_3$CH$_2$)$_3$</td>
<td>184–170 (5 mm)</td>
<td>0.8701</td>
<td>1.4284</td>
<td>120</td>
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<tr>
<td>Triheptyloxysilane</td>
<td>HSi(OCH(CHOH)$_3$CH$_2$)$_3$</td>
<td>194–196 (5 mm)</td>
<td>0.8714 (26°)</td>
<td>1.4380</td>
<td>120</td>
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<tr>
<td>Triethoxybutyoxysilane</td>
<td>HSi(OC$_2$H$_5$)$_3$</td>
<td>175–177 (14 mm)</td>
<td>1.158 (26°)</td>
<td>1.5836</td>
<td>120</td>
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<tr>
<td>Ethoxytributoxy- silane</td>
<td>HSi(OCH(CHOH)$_3$CH$_2$)$_3$</td>
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<tr>
<td>Dipentyloxysilane</td>
<td>HSi(OC$_2$H$_5$)$_3$</td>
<td>146–138 (18 mm)</td>
<td>1.150 (18 mm)</td>
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<td>Tri-sec-butoxy- silane</td>
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<td>117–118 (2 mm)</td>
<td>1.184 (21°)</td>
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<td>Tri-F-chloroethoxy- silane</td>
<td>HSi(OCH(CHOH)$_3$CH$_2$)$_3$</td>
<td>70–75 (45 mm)</td>
<td>1.2866</td>
<td>1.1577</td>
<td>120</td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Boiling Point, °C; d) Specific Gravity, $d_4^{25}$; e) Refractive Index, $n_D^{1^o}$; f) Bibliography

have not been isolated). The average number of structural units in the chain in the initial stage of hydrolysis strictly corresponds to the molar proportion of the

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water used in the reaction (provided it is added slowly enough), and may be found by the formula:

\[
\frac{x}{n} = \frac{n}{m}
\]

where \(x\) = average number of silicon atoms in the molecule;
\(n\) = number of mols of ester;
\(m\) = number of mols of water.

Table 27

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c)°C</th>
<th>d)</th>
<th>e)</th>
<th>f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexaethoxydisiloxane</td>
<td>((\text{C}_2\text{H}_4\text{O})_6\text{Si}_2\text{O})</td>
<td>153–161</td>
<td>334</td>
<td>80.0</td>
<td>46</td>
</tr>
<tr>
<td>Icosaethoxytetrasiloxane</td>
<td>((\text{C}_2\text{H}<em>4\text{O})</em>{16}\text{Si}_4\text{O}_2) (3 mm)</td>
<td>208–212</td>
<td>603</td>
<td>74.0</td>
<td>46</td>
</tr>
<tr>
<td>Tetradecaethoxyhexasiloxane</td>
<td>((\text{C}_2\text{H}<em>4\text{O})</em>{16}\text{Si}_6\text{O}_4) (0.004 mm)</td>
<td>242–247</td>
<td>869</td>
<td>70.0</td>
<td>46</td>
</tr>
<tr>
<td>Hexamethoxydisiloxane</td>
<td>((\text{C}_2\text{H}_4\text{O})_6\text{Si}_2\text{O})</td>
<td>195–205</td>
<td>256</td>
<td>—</td>
<td>119</td>
</tr>
<tr>
<td>Decamethoxytetrasiloxane</td>
<td>((\text{C}_2\text{H}<em>4\text{O})</em>{12}\text{Si}_6\text{O}_4) (0.004 mm)</td>
<td>170–195</td>
<td>473</td>
<td>—</td>
<td>119</td>
</tr>
<tr>
<td>Dodecamethoxypentasiloxane</td>
<td>((\text{C}_2\text{H}<em>4\text{O})</em>{15}\text{Si}_5\text{O}_4) (12 mm)</td>
<td>207–215</td>
<td>573</td>
<td>—</td>
<td>119</td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Boiling Point, °C; d) Molecular Weight; e) Ethylx Value; f) Bibliography

When water is introduced in an amount close to 1 mol per mol of tetraethoxysilane, the formula ceases to hold, owing to the formation of three-dimensional molecules and to the considerable increase in the velocity of reaction.

Figure 7 shows a graph of the variation of the rate of hydrolysis of tetraethoxysilane (Bibl.47) at a temperature of 65–70°C (4 mol of water were added to 1 mol of tetraethoxysilane). As will be seen from the graph, after hydrolysis of about 94% of the total number of ethoxyl groups, the process of hydrolysis slows
down considerably.

In the case of the gradual introduction of the water into the mixture, the growth of the molecules takes place not only on account of the lengthening or branching of the siloxane chain, but also on account of the cross-linking of the molecules by siloxane bridges and the formation of a polymer of spatial structure. As the number of ethoxy groups decreases, the probability of an effective collision with the molecule of water also decreases, and more and more water not participating in the hydrolysis reaction remains. Figure 8 shows the viscosity of tetraethoxysilane plotted against the amount of water added. When 2 mols of water are added to 1 mol of tetraethoxysilane, the mixture still maintains constant viscosity for many months (if there are no traces of acid present). When 4 mols of water are added, the viscosity of the mixture increases very slowly (Bibl.48), and it is only when
8 mols of water to 1 mol of tetraethoxysilane are used that the viscosity rises rather rapidly. The hydrolysis leads ultimately to gelation, owing to the formation of spatial high-molecular polysiloxane, with a certain number of hydroxyl and ethoxy groups, and which firmly adsorbs water and alcohol.

If the process of hydrolysis is conducted rapidly, by pouring an excess of water into a dilute solution of the ester, the character of the hydrolysis is substantially modified (Bibl.49). In studying a solution containing 1.88 mol of tetraethoxysilane, 5.32 mols of water, and 0.000155 mol of catalyst (HCl) to the liter, only high molecular non-volatile polymers and an insignificant amount of hexaethoxydisiloxane were found in the hydrolysis product. Other intermediate products of hydrolysis were found in the mixture. In connection with the above, the following mechanism of the process may be proposed. In its first stage, the process leads to the formation of hexaethoxydisiloxane. The velocity constant of hydrolysis of disiloxane is somewhat less than that of tetraethoxysilane, but the presence of a considerable number of ethoxy groups in the molecules increases the probability of the formation of compounds with two hydroxyl groups, of the type $\text{HO(C}_2\text{H}_5\text{O)}_2\text{SiO}_2\text{Si(OC}_2\text{H}_5\text{)}_2\text{OH}$.

The velocity of the condensation process considerably exceeds the velocity of hydrolysis, and such a compound can easily form not only the trimer, but also a higher-molecular product. The trimer has a velocity constant of hydrolysis that is only slightly different from that of the dimer. But the probability of the formation of a high-molecular compound from it is still greater. Thus the number of low-molecular products of partial hydrolysis in the process of hydrolysis is sharply reduced, and the principal reaction product consists of space polymers of high molecular weight.

**Hydrolysis of Tetraethoxysilane in an Acid Medium**

The most important factor that determines the kinetics and mechanism of the process of hydrolysis, as well as the structure and properties of the end products,
is the pH value of the medium. Under the action of 12 N HCl on a solution of tetra-
methoxysilane, hydrolysis proceeds immediately, and a large quantity of heat is
liberated, forming a gel. The conduct of the hydrolysis process in dilute solutions
in the presence of dilute acids has allowed a rather detailed study of the kinetics
of the hydrolysis process (Bibl.48). This study was made by means of periodic
determinations of the alcohol and water contents of the reaction mixture obtained on
mixing dilute HCl with a solution of tetraethoxysilane in dioxane, and also in
methanol and ethanol. The water content in the mixture was determined by titration
with Fischer's reagent, and the alcohol content by distilling it off from the reac-
tion product and determining the ethoxy groups in the distillate (cf. Table 28).

It will be seen from Table 28 that the rate of hydrolysis strongly depends on
the acidity of the medium. When the acidity is reduced below 0.005 mols to the
liter, the rate of hydrolysis is sharply retarded, while when the acidity falls
below 0.003 mols to the liter, the process of hydrolysis does not proceed to comple-
tion, even in hundreds of hours.

An indicator used to evaluate the influence of the acidity of the medium on the
course of the hydrolysis process is the quantity of water consumed during the pro-
cess of hydrolysis, that is, the difference between the number of mols of water en-
tering into the hydrolysis reaction

$$-\text{Si-O-C}_2\text{H}_4 + \text{H}_2\text{O} \rightarrow -\text{Si-OH} + \text{C}_2\text{H}_5\text{-OH}$$

and the number of molecules of water liberated on condensation according to the
reaction

$$-\text{Si-OH} + \text{HO-Si-} \rightarrow -\text{Si-O-Si} + \text{H}_2\text{O}$$

Figure 9 shows the kinetics of variation of the quantity of water consumed as
Table 28
Hydrolysis of Tetraethoxysilane in Dioxane

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c)</th>
<th>d)</th>
<th>e)</th>
<th>f)</th>
<th>g) %</th>
<th>h) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.063</td>
<td>0.1924</td>
<td>1.432</td>
<td>2</td>
<td>100</td>
<td>86</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.0281</td>
<td>0.2045</td>
<td>1.392</td>
<td>1.20</td>
<td>97</td>
<td>91</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.0354</td>
<td>0.2132</td>
<td>1.470</td>
<td>6.40</td>
<td>100</td>
<td>97</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.0120</td>
<td>0.168</td>
<td>1.594</td>
<td>160</td>
<td>100</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.0022</td>
<td>0.358</td>
<td>2.45</td>
<td>500</td>
<td>90</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.0016</td>
<td>0.2903</td>
<td>1.207</td>
<td>1</td>
<td>40</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.000022</td>
<td>0.2132</td>
<td>1.249</td>
<td>170</td>
<td>88</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

a) Experiment Number; b) Initial Concentration of Solution, mol/liter; c) HCl; d) Tetraethoxysilane; e) Water; f) Time, Hours-min.; g) Degree of Hydrolysis, \%; h) Condensation of Hydrolysis Product, \%

It has been found experimentally that the hydrolysis reaction at HCl concentrations of the order of 0.003 mol per liter is a second-order reaction. Adopting the notation: $S_{\text{e}o}$ = initial concentration of tetraethoxysilane, $M_{\text{e}o}$ = initial concentration of water, and $x$ = number of mols of tetraethoxysilane entering into reaction, the general equation of the kinetics of the process may be written as follows:

$$\frac{dx}{dt} = K (M_{r} - x) \left(2S_{r} - x\right)$$

or, after integration:

$$\log \frac{M_{r} - x}{2S_{r} - x} = K \cdot \frac{M_{e} - 2S_{r}}{2S_{r}} \cdot - \log \frac{M_{r}}{2S_{r}}$$

As a result of the incompleteness of the processes of condensation, the total quantity of water ($2x$), used in the reaction of hydrolysis will not be equal to the difference between the quantity of water introduced and that of the water remaining in the medium at time $t$, and it is necessary to have a factor related to the incom-
pleteness of the condensation:

\[ 2x = 2 \frac{y}{x} (M_f - M_i) \]

Knowing the value \( a \) for a given value of the acidity, the relation of the value of \( \log \frac{M_c - x}{2S_t o - x} \) with the time in the form of straight lines (Fig.10), the velocity constant of reaction being determined for each value of the acidity by an equation into which the value of the angle of inclination of the straight line, \( \beta \), enters:

\[ K = \frac{2.3030 \log b}{M_f - 2a}. \]

Calculations of \( K \) show that the log of the value of the velocity constant of reaction is a regular function of the acidity of the medium (Fig.11). This relation may be expressed by the following equation:

\[ \log K = \log [HCl] + \log 0.051. \]

Thus the value of the ratio between the reaction constant and the HCl concentration is a constant, which for a solution of tetraethoxysilane in dioxane at 20°C, is equal to 0.051.

A comparison of the values of the velocity constant at 20°C and 45.3°C made it possible to calculate the energy of activation according to the well known equation
When the temperature is increased from 20°C to 45.3°C, the rate of hydrolysis increases by a factor of 10.

\[ Q = \frac{d \ln K}{dT} \quad RT^Q = 6.8 \text{ kcal/mol} \]

Fig. 10 - Relation between Rate of Hydrolysis of Tetraethoxysilane in Dioxane and the Acidity of the Medium:
1 - 0.063 mol HCl to 1 liter of solution;
2 - 0.0281 mol HCl to 1 liter of solution;
3 - 0.0053 mol HCl to 1 liter of solution;
4 - 0.0016 mol HCl to 1 liter of solution;
5 - 0.000022 mol to 1 liter of solution;

a) Time, hours

Fig. 11 - Relation between Velocity Constant of Hydrolysis of Tetraethoxysilane and Acidity of Medium
a) log of molar concentration of HCl;
b) log of velocity constant of reaction

A study of the process of hydrolysis shows that it proceeds in an alcoholic medium as it does in dioxane (Bibl.48) (Table 29). The same value obtained for the velocity constant indicates that the process of esterification does not take place under these conditions.

The mechanism of hydrolysis in an acid medium has been connected with the formation of the oxone compound, which reacts with the ester according to the formula:
\[
\begin{align*}
\text{HOH} & \quad \text{HCl} \\
\text{Si-OR} + \text{H}_2\text{O} & \quad \rightarrow \text{Si--OR} \quad \rightarrow \text{SiOH} + \text{ROH} + \text{HCl} \\
\end{align*}
\]

or:

\[
\begin{align*}
\text{H}_2\text{O} + \text{Si(OR)} + \text{HCl} & \quad \rightarrow \text{H}_2\text{O}:\text{Si-OR} \quad \rightarrow \text{SiOH} + \text{ROH} + \text{HCl}
\end{align*}
\]

Table 29
Hydrolysis of Tetraethoxysilane in Methanol

<table>
<thead>
<tr>
<th>HCl</th>
<th>a)</th>
<th>c)</th>
<th>d)</th>
<th>e)</th>
<th>f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0034</td>
<td>0.624</td>
<td>2.32</td>
<td>0.20</td>
<td>0.054</td>
<td></td>
</tr>
<tr>
<td>0.0016</td>
<td>0.210</td>
<td>1.07</td>
<td>0.104</td>
<td>0.065</td>
<td></td>
</tr>
<tr>
<td>0.0037</td>
<td>0.624</td>
<td>1.16</td>
<td>0.12</td>
<td>0.042</td>
<td></td>
</tr>
</tbody>
</table>

a) Initial concentration, mol/liter; b) HCl; c) Tetraethoxysilane; d) Water; e) Velocity constant of reaction, \( K \times 10^3 \); f) Ratio between reaction constant and HCl concentration, \( K/\text{[HCl]} \)

The reaction velocity depends on the velocity of rearrangement of the bonds or of the addition of the hydroxyl group to the tetraethoxysilane molecule. In both cases, the velocity is determined by the product of the concentrations of water and hydrogen chloride.

The preference may be given to the first reaction, as a bimolecular reaction.

As a result of a study of the kinetics of the process (Table 28), the conclusion may be drawn (Bibl.48) that the velocity of the process of condensation in an acid medium considerably exceeds the velocity of hydrolysis, so that it is not possible to isolate hydroxyl-containing products of hydrolysis from the mixture.

In a weakly acid medium, when the acidity is reduced, the velocity of hydrolysis is also reduced, so that the possibility of complete condensation of the...
hydroxyl groups as soon as they are formed is increased, and at an acidity of less than 0.003 mol per liter, in the absence of a large excess of water, the process of hydrolysis in dilute solution leads to the formation of polymers not containing hydroxyl groups.

An increase in the temperature of hydrolysis favors a greater degree of completion of the processes of condensation, thus, at 20°C and 45.5°C, other conditions being equal, the degree of condensation is respectively 89% and 93%, but even at a temperature above 50°C, the condensation still does not proceed to completion.

In contrast to the hydrolysis of SiCl₄, the formation of cyclic compounds \[ \{(C₂H₅O)₂SiO\}_x \], with molecular sizes 11, 6, and 4.1 Å, is noted on the hydrolysis of tetraethoxysilane in an acid medium.

The stability of the sol of the hydrolysis products depends mainly on three factors. The principal factor is the acidity of the medium. When the acidity is reduced below 0.002 mol per liter, the velocity of gelation rapidly rises. The other factors are the concentration of the starting monomer in the solution, and the amount of unreacted monomer. When the concentration of the hydrolysis product increases, gelation is accelerated, but the presence of unreacted tetraethoxysilane in the mixture stabilizes the sol of the hydrolysis product.

If the solvent is removed from the products of incomplete hydrolysis of tetraethoxysilane, then an infusible compound (a powder outwardly resembling silica gel) containing a few percent of ethoxy groups, is formed. This powder is completely insoluble. A study of the films obtained by evaporating solutions of hydrolyzed tetraethoxysilanes on a mercury surface by X-ray diffraction shows the structure of the polymer to be similar to that of frozen solid tetraethoxysilane. It follows from this that the end-groups of polysiloxane are ethoxy groups.

Hydrolysis of Tetraethoxysilane in an Alkaline Medium

The presence of alkali in the solution being hydrolyzed likewise favors the acceleration of the process of hydrolysis of tetraethoxysilane, but the character of
the hydrolysis in alkaline medium is somewhat different. The results of hydrolysis in a medium of methanol, ethanol, or dioxane in the presence of an alkali are summarized in Table 30.

Table 30
Hydrolysis of Tetraethoxysilane in Various Solvents in the Presence of Alkalis

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c)</th>
<th>d)</th>
<th>e)</th>
<th>f)</th>
<th>g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>0.047</td>
<td>0.235</td>
<td>1.06</td>
<td>0-03</td>
<td>0.11</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.766</td>
<td>0-09</td>
<td>0.99</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.597</td>
<td>0-25</td>
<td>1.72</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.557</td>
<td>0-53</td>
<td>1.89</td>
<td>4.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.520</td>
<td>10-00</td>
<td>2.04</td>
<td>4.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0185</td>
<td>1.25</td>
<td>2.44</td>
<td>0</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.29</td>
<td>0-04</td>
<td>0.256</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.12</td>
<td>0-21</td>
<td>0.505</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.81</td>
<td>2-15</td>
<td>1.70</td>
<td>3-40</td>
<td>0.590</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.13</td>
<td>18-00</td>
<td>0.97</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.0163</td>
<td>0.2305</td>
<td>0.985</td>
<td>0</td>
<td>0.41</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.89</td>
<td>2-25</td>
<td>0.65</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.835</td>
<td>23-25</td>
<td>0.93</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.77</td>
<td>47-00</td>
<td>1.14</td>
<td>2.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.72</td>
<td>119-00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dioxane</td>
<td>0.035</td>
<td>0.236</td>
<td>2.0</td>
<td>3-00</td>
<td>0.75</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>0.0145</td>
<td>0.2144</td>
<td>1.62</td>
<td>240-00</td>
<td>0.35</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td>0.0083</td>
<td>0.236</td>
<td>1.92</td>
<td>300</td>
<td>0.3</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>0.00391</td>
<td>0.236</td>
<td>1.67</td>
<td>300</td>
<td>0.3</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>0.000205</td>
<td>0.236</td>
<td>1.424</td>
<td>30000</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.220</td>
<td>0.846</td>
<td>0</td>
<td>0</td>
<td>0.64</td>
<td>-</td>
</tr>
<tr>
<td>Ammonia</td>
<td>0.220</td>
<td>0.855</td>
<td>0-10</td>
<td>0</td>
<td>0.75</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.222</td>
<td>0.858</td>
<td>0-10</td>
<td>0</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.227</td>
<td>1.024</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.144</td>
<td>0.227</td>
<td>1.602</td>
<td>22-30</td>
<td>0.114</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.144</td>
<td>0.227</td>
<td>0.946</td>
<td>147-00</td>
<td>0.365</td>
<td>-</td>
</tr>
</tbody>
</table>

a) Solvent; b) Composition of Mixture Hydrolyzed, mol/liter; c) Alkali; d) Tetraethoxysilane; e) Water; f) Duration of Hydrolysis, Hours–minutes; g) Number of mols per mol of Tetraethoxysilane; h) Of Water Consumed; i) Of Alcohol Liberated

The data presented in Table 30 indicates the strong dependence of the course
of the condensation process on the pH of the medium and on the nature of the solvent. Hydrolysis in an alkaline medium in general proceeds more slowly than in an acid medium, and requires the presence of relatively large amounts of alkali. Hydrolysis in methanol proceeds most rapidly. It is noted that an increase in the concentration of tetraethoxysilane involves the precipitation of the polymeric hydrolysis product in the form of a white precipitate. The same thing is observed in solutions in ethanol, although the rate of reaction in such case is somewhat slower. In dioxane, the reaction proceeds most slowly of all, and at high alkali concentrations two layers are formed, a solution of the monomer in dioxane, and an aqueous alkaline sol of the hydrolysis product.

At alkali concentration of the order of $10^{-3}$ mol per liter, the process of hydrolysis in dilute solutions is practically completely stopped.

Ammonia and pyridine catalysed the hydrolysis reaction only when present in considerable quantities, while, in ammoniacal solutions, the immediate condensation of the hydrolysis products takes place and the polymer is almost immediately thrown down in the form of a white flocculent precipitate.

The order of the reaction was determined by comparing the time necessary to reach a certain degree of hydrolysis at different concentrations of the reagents. It was found that at low concentrations of the reagents, the reaction of hydrolysis of tetraethoxysilane is of the first order, and, consequently, may be described by the following equation:

$$2.303 \log (2S_p - x) = -K + C$$

where K is the velocity constant of reaction, whose value is close to that of the reaction of acid hydrolysis (cf. page 268 and Table 31).

In contrast to acid hydrolysis, the rate constant of alkaline hydrolysis is not proportional to the concentration of OH ions, but is a linear function of it:
\[
\frac{K}{K'} = 3.1 \left[ \frac{[\text{NaOH}]}{[\text{NaOH}]} \right]^2 - 2.1
\]

Table 31

Hydrolysis of Tetraethoxysilane in an Alkaline Medium

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c)</th>
<th>d) $K/[\text{NaOH}]$</th>
</tr>
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<tbody>
<tr>
<td>0.0347</td>
<td>0.235</td>
<td>1.67</td>
<td>0.047</td>
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<tr>
<td>0.0130</td>
<td>0.162</td>
<td>1.70</td>
<td>0.029</td>
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</table>

a) Concentration of Alkali, mol/liter; b) Concentration of Tetraethoxysilane, mol/liter; c) Velocity Constant of Hydrolysis, $K \times 10^3$; d) Ratio of Velocity Constant of Hydrolysis to Concentration of alkali, $K/[\text{NaOH}]$

This relation is graphically represented in Fig. 12 (cf. also Table 31).

In the case of more concentrated solutions, the rate constant falls sharply, and the relative time necessary to reach a certain degree of hydrolysis at different concentrations is different. At a concentration of tetraethoxysilane in the mixture of 0.936 mols per liter of solution, the process of hydrolysis is a first order reaction until 30% of the reaction has been completed. At a tetraethoxysilane concentration of 1.25 mol per liter, the velocity of the reaction decreases sharply, and a precipitate is thrown down immediately after the beginning of the hydrolysis.

The polymer obtained in an alkaline medium has a structure different from that of the product of acid hydrolysis. In the former case, the addition of monomer does not exert a stabilizing influence on the sol of the hydrolyzate. It may be postulated that, together with the intermolecular condensation of the hydrolysis products:

\[
\text{Si-OH} + \text{HO-Si}^- \rightarrow \text{Si-O-Si}^- + \text{H}_2\text{O}
\]
the reaction of formation of silanolate groups also takes place:

\[ \text{Si-OH} + \text{NaOH} \rightarrow \text{Si-ONa} + \text{H}_2\text{O} \]

This reaction probably takes place on the surface of the polymer, which results in the slowing of the process of dissolution. Obviously the separation of phases in hydrolysis in dioxane is also connected with this.

As for the mechanism of the process of alkali hydrolysis, here the existence of nucleophilic substitution is postulated, but, in contrast to the process of acid hydrolysis, the rate of reaction increases with increasing dielectric constant of the medium, which is obviously connected with dissociation. The following mechanism of nucleophilic substitution is proposed:

\[ \text{OH}^- \rightarrow \text{SiOR} \rightarrow \text{HO} : \text{SiOR}^- \rightarrow \text{HOSi}^- + \text{OR}^- \]

Here, the obvious factor determining the velocity of reaction is the cleavage of the nucleophilic complex.

**Hydrolysis of Other Tetraalkoxysilanes**

The processes of hydrolysis of various esters of orthosilicic acid differ in reaction velocity and in the structure of the end product, but fundamentally the mechanism of the process is analogous to what has just been described.

From the mixture formed under the action of insufficient water on tetramethoxysilane, individual polymethoxysiloxanes containing from 2 to 10 silicon atoms in the siloxane chain have been isolated. The hydrolytic cleavage of the methoxy group proceeds more easily than that of the ethoxy group. On introduction of 1 mol of water per mol of tetramethoxysilane (Bibl.49), the average molecular weight of the hydrolysis products (which obviously have a branched or linear structure) is as
much as 10,000. The gel obtained as a result of the hydrolysis of tetramethoxysilane contains an insignificant number of methoxy groups.

The hydrolysis of the isopropyl and isobutyl esters of orthosilicic acid proceeds at a lower intensity. The initial hydrolysis products have been obtained (Bibl.49) by reacting SiCl₄ with a mixture of an alcohol and the calculated quantity of water; for instance, with a ratio of 0.5 mol of water per mol of SiCl₄, the principal reaction product is the hexaalkoxydisiloxane. It is very interesting that together with linear polyalkoxyxiloxanes, it has also been possible to obtain cyclic polysiloxanes, for instance tetramers [OSi(OR)₂]₄ and the higher siloxanes, which according to the author's opinion, have the structure of condensed tetrasiloxane rings. These compounds were the first siloxane hydrolysis products not containing the Si-C bond to be isolated in the free state. On heating the hydrolysis product of the isopropyl ester of orthosilicic acid, processes of condensation occur, with cleavage of diisopropyl ester or of its decomposition products, isopropyl alcohol and propylene:

\[
-\text{Si}-\text{OR} + \text{ROS}-\text{O} \rightarrow -\text{OSi}-\text{OSi(O) + R}_2(\text{)}
\]

In the case of octaisopropoxycyclotetrasiloxane, the process obviously proceeds with the formation of cross-linked rings, and also, perhaps, of a certain quantity of condensed rings of the type:

![Graph](image-url)
The further process of condensation cannot be exactly described on the basis of these experimental data. Only certain general considerations may be expressed, to the effect that the cyclic products so formed are joined together through the Si–O–Si siloxane bonds with liberation of an ester on account of the alkoxy groups. The formation of complex mixtures of polymeric homologs of linear, cyclical, or cross-linked structure is the most probable.

Hydrolysis of Higher Tetraalkoxysilanes in the Presence of Catalysts

A study of the process of the hydrolysis of higher tetraalkoxysilanes in an acid medium (Bibl.49) shows that the regularities pointed out for tetraethoxysilane also hold for the higher tetraalkoxysilanes. The process of hydrolysis is rather accurately described by the equations for a second-order reaction, the rate constant varying approximately in proportion to the hydrogen-ion concentration.

Thus, to evaluate the velocities of hydrolysis of various tetraalkoxysilanes, the ratio between the velocity constant of hydrolysis and the hydrogen ion concentration may be used. The equation for the second-order reaction reflecting the course of the process of hydrolysis (cf. page 269) may in this case be written as follows:

\[ \frac{M_p - x}{2S_p} = \text{[H]} K \frac{M_p - 2S_p}{2.303} - \log \frac{M_p}{2S_p} \]

where

F-TS-9191/V 276
\[
K = -\frac{K}{[H^+]}\]

If the equation is written in the following form:

\[
\frac{1}{[H^+]} \left( \log \frac{M_{t^0} - x}{2S_{t^0} - x} - \log \frac{M_{t^0}}{2S_{t^0}} \right) = K \frac{M_{t^0} - 2S_{t^0}}{2,303}
\]

and the time-dependence of the quantity

\[
\frac{1}{[H^+]} \left( \log \frac{M_{t^0} - x}{2S_{t^0} - x} - \log \frac{M_{t^0}}{2S_{t^0}} \right)
\]

is plotted on the graph (Fig. 13) then we shall have a family of curves, by using the angle of inclination of which, by analogy to the preceding, the values of the velocity constant of reaction can easily be calculated for various tetraalkoxysilanes.

Table 32
Hydrolysis of Tetrahexylsiloxane

<table>
<thead>
<tr>
<th>a)</th>
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<td></td>
</tr>
<tr>
<td>0.0244</td>
<td>0.238</td>
<td>1.292</td>
<td>2.15</td>
<td>0.00888</td>
<td></td>
</tr>
<tr>
<td>0.0765</td>
<td>0.236</td>
<td>1.352</td>
<td>0.65</td>
<td>0.0081</td>
<td></td>
</tr>
</tbody>
</table>

a) Initial Concentration, mol/liter; b) HCl; c) Tetrahexylsiloxane; d) Water; e) Velocity Constant of Reaction, \(K \times 10^k\); f) Ratio between Velocity Constant of Reaction and Hydrogen Ion Concentration, \(K/[H^+]\)

The variation in the value of the velocity constant is determined primarily by the molecular weight of the alkoxyl group (by the number of carbon atoms, cf. Fig. 14), and also by its structure. The presence of branches in the carbon chain of the...
alkoxy group sharply affects the velocity of hydrolysis of the lower tetraalkoxysilanes, and, to a lesser extent, that of the higher tetraalkoxysilanes (more than 10 carbon atoms), which indicates the existence of steric hindrance as the factor which, to a certain extent, determines the course of the process of hydrolysis.

![Graph](image1)

**Fig. 13** - Dependence of Velocity of Hydrolysis of Tetraalkoxysilanes in an Acid Medium on Size and Structure of the Alkoxy Group

1. \( \text{Si(OCH}_2\text{CH}_3\text{)}_4 \)
2. \( \text{Si(OCH}_3\text{)}_2\text{H}_2\text{Si(OCH}_3\text{)}_2 \)
3. \( \text{Si(OCH}_3\text{)}_3\text{H} \)
4. \( \text{Si(OCH}_2\text{CH}_2\text{CH}_2\text{)}_2\text{O} \)

a) Time, hours

A study of the process of hydrolysis of tetraalkoxysilanes containing both higher and lower alkoxy groups is very interesting. In this case, the above consideration would lead us to expect the formation mainly of lower alcohols during the process of hydrolysis. But the experimental results do not confirm this. We present, as an example, the hydrolysis of dihexyloxydiethoxysilane (cf. Table 33).

For tetraalkoxysilanes containing unlike alkoxy groups, the following values of the velocity constant of hydrolysis, related to unit concentration of ions, \( K/[H^+] \),

![Graph](image2)

**Fig. 14** - Velocity Constant of Hydrolysis of Tetraalkoxysilanes vs. Number of Carbon Atoms in R Group:

1. \( \text{Si(OR)}_4 \)
2. \( \text{H}_2\text{Si(OR)}_2(\text{C}_2\text{H}_5\text{O})_2 \)

a) Number of carbon atoms in R group;
b) Velocity constant of hydrolysis, \( K \times 10^3 \)
were found.

Table 33
Hydrolysis of Diethyloxydiethoxysilane

<table>
<thead>
<tr>
<th>a)</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>HCl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.00130</td>
<td>1.40</td>
<td>0.377</td>
<td>1.38</td>
<td>1.29</td>
</tr>
<tr>
<td>Ethanol + Hexanol</td>
<td>0.00136</td>
<td>1.51</td>
<td>0.560</td>
<td>1.25</td>
<td>1.38</td>
</tr>
</tbody>
</table>

a) Solvent; b) Initial Concentration, mol/liter; c) HCl; d) Water; e) Dihexyloxydiethoxysilane; f) Number of mols of Alcohol Formed per mol of Ester;

g) Hexanol; h) Ethanol

Table 34
Ratio of Velocity Constant of Hydrolysis of Various Alkoxy silanes to Hydrogen Ion Concentration (K/[H⁺])

<table>
<thead>
<tr>
<th>a)</th>
<th>R=CH₃</th>
<th>R=CH₂CH₂CH₃/H(CH₂)₂</th>
<th>R=CH₂CH₂CH₂CH₃/H(CH₂)₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(OR)₄</td>
<td>0.008</td>
<td>0.008</td>
<td>0.008</td>
</tr>
<tr>
<td>C₃H₅OSi(OR)₂</td>
<td>0.011</td>
<td>0.011</td>
<td>0.011</td>
</tr>
<tr>
<td>(C₆H₅O)₂Si(OR)₂</td>
<td>0.50</td>
<td>0.0015</td>
<td>0.00095</td>
</tr>
<tr>
<td>(C₆H₅O)₃Si(OR)</td>
<td>0.50</td>
<td>0.0015</td>
<td>0.00085</td>
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</table>

*For Si(OC₂H₅)₄, K/[H⁺] = 0.051.

a) Formula

These data allow us to draw the conclusion that the presence of unbranched alkoxy groups in the compound (cf. Table 34), slows the process of hydrolysis only in the case where there are more than two of them in the molecule. If their number is exactly two, then the velocity of hydrolysis of a tetraalkoxysilane with two branched and two ethoxy alkoxy groups holds close to the velocity of hydrolysis of the
corresponding branched tetraalkoxysilane. From these data the conclusion may be
drawn that the velocity of hydrolysis is completely determined by the screening ac-
tion of the radicals of the alkoxyl groups, or, in other words, that the fundamental
rate-determining factor for the process is the difficulty of the water molecule or
hydroxonium ion penetrating to the oxygen of the ether bond Si–OC. After the
attachment of the water or hydroxonium, however, the further course of the reaction,
the authors assert, does not depend on the structure of the alkoxy group, or depends
on it only to an insignificant extent, and the relative stability of the Si–OC bond,
depending on the presence of these or those radicals, then affects the ether=bond
disruption rate, itself, only to an insignificant extent.

In contrast to the processes of hydrolysis of tetraethoxysilane, in the
hydrolysis of the higher tetraalkoxysilanes, the processes of reesterification of
the free hydroxyl groups by the alcohols, which are solvents, and consequently are
present in considerable excess, does have a certain importance.

The tetraphenoxysilanes are hydrolyzed with relative ease by water. At the
very instant of contact between tetraphenoxysilanes and water, polyphenoxysiloxanes
are formed, and if alcohol is added, or on boiling with water, hydrolysis proceeds
practically to completion. For instance, when 0.1079 g of tetraphenoxysilane is
boiled with 150 g of water, 98.6% of the theoretical quantity of phenol is formed.
The considerable acceleration of the hydrolytic processes is caused usually by the
presence of additional functional groups in the molecule of the ester of ortho-
silicic acid (Bibl.102), for instance of chlorine in Si(OC₂H₄Cl)₄ or of the ether
group in Si(OC₂H₄OR)₄.

The rate of condensation of the hydrolyzates of the higher tetraalkoxysilanes,
and the hydrolyzates of tetraethoxysilane, both in dilute solutions, are close to-
gether; the final stage of the condensation decreases with increasing acidity and
with the increase in the molecular weight of the alkoxy groups (cf.Table 35).

On the hydrolysis of esters whose alkoxy groups have unwieldy radicals, poly-
mers containing hydroxyl groups are formed. This is obviously related to steric hindrance as well, for the long carbon chains, and even more, branched or cyclic chains, prevent the approach of the hydroxyl groups, thus hindering the process of condensation. Thus, for example, the polymeric products of the hydrolysis of cyclohexyloxychlorosilanes always contain free hydroxyl groups, and it is possible to run the reaction according to the formula

\[ (C_6H_{11}O)_2SiCl_2 \rightarrow [(C_6H_{11}O)_2SiO]_x \]

only when ether solutions of dicyclohexyldichlorosilane are reacted with dry silver carbonate (Bibl.50), thus forming the cyclic trimer and tetramer. From tricyclohexyloxychlorosilane under similar conditions, hexacyclohexyloxydisiloxane is obtained:

\[ 2 (C_6H_{11}O)_2SiCl + AgCl \rightarrow (C_6H_{11}O)_2SiOSi(OC_6H_{11})_2 + 2AgCl + CH_4 \]

and from cyclohexyloxytrichlorosilane, the polymer [Si(OC_6H_{11})O_{1.5}]_x, whose structure recalls that of the compounds obtained by the complete hydrolysis and condensation of alkyltrichlorosilanes. In this case, when the silver carbonate used for the reaction contains traces of moisture, hydroxypolyalkoxysiloxanes are formed.

### Hydrolysis of Polyalkoxysiloxanes

In studying the kinetics of the process of hydrolysis of polyalkoxysiloxanes, the basic propositions established for the hydrolysis of the tetraalkoxysiloxanes were confirmed (Bibl.49). The velocity constants of hydrolysis of the alkoxyl...
groups and the ratio $K/[H^+]$ decrease for the polymers with their increasing molecular weight, which is illustrated by Fig.15, and by the data of Table 36 on the hydrolysis of polyethoxysiloxanes.

Table 36

<table>
<thead>
<tr>
<th>Hydrolysis of Polyethoxysiloxanes</th>
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**Polyethoxysiloxane in which the ratio $\frac{[OC_2H_5]}{[S]} = 1.585$.**

a) Starting Compound; b) Initial Concentration, mol/liter; c) HCl; d) Water; e) $OC_2H_5$; f) $K/[H^+]$

Figure 16 shows that, with lengthening of the polysiloxane chain, the value of the constant decreases, this decrease becoming smaller and smaller and ultimately being stabilized when it reaches about 1/6 the value of the constant for the monomer. It must be noted that the variation of the velocity constant of hydrolysis of polysiloxanes, as a function of the siloxane chain length, is considerably smaller than the variation of the velocity constant of hydrolysis of tetraalkoxysilanes as a function of the increase in alkoxy-group length. This confirms the above hypothesis that the rate of hydrolysis is primarily determined by the ease with which water or a nucleophilic reagent penetrates to the ether oxygen, for which a long organic group is naturally a greater obstacle than a siloxane chain.

In a study of the hydrolysis of polyisopropoxysiloxane in the presence of a normal solution of ammonia, it was found that for different polysiloxanes, the
process proceeds with approximately the same velocity (Fig.17). In the absence of a catalyst, the velocity of hydrolysis decreases sharply.

![Graph](image1)

**Fig.15** - Relation between the Velocity of Hydrolysis of Polyethoxysiloxanes in Dioxane and the Composition of the Polymers:

1 - 60% Monomer; 40% Dimer; 2 - 68% Monomer; 32% Trimer; 3 - Trimer; 4 - Polymer in which the Ratio \( \frac{C_2H_5O}{Si} = 1.585 \)

**Fig.16** - Relation between Velocity of Hydrolysis of Alkoxy Groups in Polyethoxysiloxanes and the Length of the Siloxane Chain

a) Monomer; b) Dimer; c) Trimer; d) Polymer

a) Time, minutes

In estimating the values of the velocity constant of hydrolysis of tetraalkoxy-silanes, it must be borne in mind that the constants represent average values determined by the velocity constants of hydrolysis of all the intermediate polysiloxanes that are formed. The reduction of the velocity constant of hydrolysis of disiloxane by comparison with that of tetraalkoxysilane is due to the exclusion of the largest component that determines the hydrolysis of the first alkoxy group, etc.

Tetraethoxysilane is of the greatest practical importance among the esters of orthosilicic acid. Most papers on the practical conduct of the process of hydrolysis and the use of the products relate to this compound. There are several different methods of hydrolysis: blowing of moist air, hydrolysis in aqueous emulsion and
in alcoholic solution. "Ethyl silicate 40", for instance, is brought to the standard viscosity and SiO₂ content by vigorous mixing with the necessary quantity of water in the presence of emulsifiers (Bibl.45).

Preparation of aqueous sol of deeply hydrolyzed tetraethoxysilane (Bibl.45). The hydrolyzed product, containing 40% of SiO₂ ("ethyldisilicate"), 20 parts by volume, is vigorously stirred for 1 hour with 4 parts by volume of 5% HCl, and 76 parts by volume of water are then added to the mixture. The sol so obtained does not coagulate for several days.

For several purposes it is convenient to use esters of orthosilicic acid hydrolyzed by prolonged heating with water at the boiling point; the product consists of a mixture of high-molecular viscous soluble polyethoxysiloxanes (Bibl.31, 100, 101).

The method of hydrolysis that is most widely used and is most reliable, however, is hydrolysis in the presence of an aqueous alcohol (usually ethanol or methanol). The most widely used catalyst for the process of hydrolysis is HCl, and its concentration in the water going to the hydrolysis ranges from 0.3 to 5% (depending on the necessary rate of hydrolysis.
and the required acidity of the end product).

Figure 18 gives a solubility diagram of the system tetraethoxysilane-denatured 94% alcohol-water (Bibl.51). The line AB corresponds to a mixture containing the

Fig.18 - Solubility Diagram for the Ternary System
Tetraethoxysilane-Alcohol-Water

a) Tetraethoxysilane; b) Alcohol; c) Water

quantity of water theoretically necessary for complete hydrolysis. The amount of water usually introduced into the reaction is somewhat smaller than that theoretically necessary, so that polysiloxane still retaining a certain number of ethoxy groups is formed, which favors adhesion and improvement of the mechanical indices of the hydrolyzate.

The maximum quantity of SiO₂ in the single-phase mixture containing the theoretical quantity of water is 17.5% (the composition of such a mixture corresponds to the point 1: 35% alcohol, 8% water, 57% tetraethoxysilane). But such a mixture is not sufficiently stable for a prolonged period. Better results are obtained when the hydrolysis is run in two stages:

(1) preparation of a partially hydrolyzed product which may be kept for any
length of time (the point 2: 73% tetraethoxysilane, 2% water, 25% alcohol);

(2) preparation of the completely hydrolyzed product.

In not less than 12 hours after the first stage of hydrolysis has been run, water is added in an amount assuring complete hydrolysis (point 3: 69% tetraethoxysilane, 8% water, 23% alcohol). The mixture is a single-phase system, since as a result of the partial preliminary hydrolysis, alcohol is formed. In a few hours, the hydrolysis is complete, and the mixture is ready for use.

We have already pointed out the advisability of using a polymeric product containing as much as 40% of SiO₂ for hydrolysis.

![Fig.19 - Solubility Diagram for the Ternary System: Ethyl silicate 40% = Alcohol-Water](image)

a) Ethyl silicate; b) Alcohol; c) Water; d) Region of mixing;

e) Region of non-mixing

Figure 19 gives a solubility diagram of a mixture of such a product with water and denatured 94% alcohol (Bibl.45). The line BC corresponds to mixtures containing theoretical quantity of water; the line AD to the solutions usually employed,
whose hydrolysis is completed by adsorption of atmospheric moisture. The following method of hydrolysis is the most rational:

(1) preparation of the partially hydrolyzed product (the composition of such a mixture corresponds to point 2: 81% of "ethyl silicate 40", 2% of water, 17% of alcohol);

(2) preparation of the completely hydrolyzed product (point 3: 76% "ethyl silicate 40", 7% of water, 17% of alcohol).

It has recently been found that in the presence of alkaline catalysts, the so-called "condensing agents", the process of hydrolysis proceeds considerably more quietly, and the final product of hydrolysis possess better mechanical properties in connection with the presence of a larger number of ethoxy groups in it. Besides this, the "condensing agents" encourage the stabilization of the partially hydrolyzed ester. A mixture containing 2% of a condensing agent is stable during prolonged storage under room conditions, and after aqueous alcohol has been introduced into it, it "sets" inside of 20 - 30 minutes. When smaller quantities of condensing agents are used, the time required for the product to "set" is lengthened.

Reaction with Organometallic Compounds

The most important chemical property of the esters of orthosilicic acid is their power, under the action of organometallic compounds, of substituting an organic radical for an alkoxy group to form substituted esters. These esters constitute one of the most important forms of intermediate product for the manufacture of organosilicon polymers.

The most important reaction of this type is the alkylation of esters of orthosilicic acid by the aid of organomagnesium compounds. The preparation of substituted esters of orthosilicic acid by this method, under industrial conditions, has become possible owing to the replacement of ethyl ether by tetraethoxysilane
The alkylation of esters of orthosilicic acid may be accomplished by two methods:

1. By preparing an organomagnesium compound from a halogen alkyl and magnesium in the presence of catalytic quantities of tetraethoxysilane, followed by a reaction with an ester of orthosilicic acid (Bibl.123):

   \[ 2RMgX + Si(OR')_4 = R_2Si(OR')_2 + 2R'OMgX \]

2. Single-phase alkylation by pouring, onto magnesium, in the theoretical proportions, a mixture of an ester of orthosilicic acid, a halogen alkyl, and a solvent.

   The latter method is considerably more convenient, since it makes it possible to prepare the desired product in better yield.

   In contrast to the alkylation of SiCl\(_4\), in the alkylation of esters of orthosilicic acid, the amount of byproducts usually formed is small, and with a proper selection of the proportions between the reagents, the reaction can be directed completely, or almost completely, toward the formation, either of monoalkylalkoxy-silanes:

   \[ Si(OR)_4 + Mg + R'X = R'Si(OR) + 2ROMgX \]

   or dialkylalkoxy-silanes:

   \[ Si(OR)_4 + 2R'X + 2Mg = R_2Si(OR)_2 + 2ROMgX \]

   When trialkylalkoxy-silanes

   \[ Si(OR)_4 + 3Mg + 3R'X = R_3Si(OR) + 3ROMgX \]

   are prepared, a considerable amount of dialkylalkoxy-silanes are also formed. On the reaction of esters of orthosilicic acid with organomagnesium compounds under
ordinary conditions of synthesis, the tetraalkyl- or tetraarylsilanes are formed in very small quantities.

Without using ethyl ether, reactions have been conducted (Bibl.53) with ethylmagnesium bromide, isopropylmagnesium bromide, isobutylmagnesium chloride, and isomagnesium chloride; the process has been conducted both in a single stage, and with the preliminary preparation of the organomagnesium compound.

Allytriethoxysilane (Bibl.54) has been prepared, using either allyl bromide (yield 55%), or allyl chloride (yield 50%). Reactions of alkylation of tetraethoxysilane in a single stage by the passage of gaseous methyl chloride or ethyl chloride through a mixture of tetraethoxysilane and magnesium under stirring, have been described. The reaction product is a mixture of mono- and dialkylalkoxysilanes (Bibl.55). The conduct of the process under pressure does not exert a substantial influence on the yield of the products (Bibl.56).

Under the action of methyldimethylsilane in ether solution, methyldimethylsilane and dimethyldiethoxysilane are formed (Bibl.57).

Vol'nov and Reutt (Bibl.58) have obtained mono- and diphenylethynylethoxysilanes without using ethyl ether:

\[
\begin{align*}
    C_2H_5Br + Mg & \rightarrow C_2H_5MgBr \\
    C_2H_5MgBr + HC\equiv CC_2H_5 & \rightarrow C_2H_5C\equiv CMgBr + C_2H_6 \\
    C_2H_5C\equiv CMgBr + Si(OCH_3)_3 & \rightarrow C_2H_5C\equiv CSi(OCH_3)_3 + C_3H_8OMgBr
\end{align*}
\]

Chotinskiy and Serezhnenkov (Bibl.59), on alkylation of tetraethoxysilane by ethereal solutions of phenylmagnesium bromide, of 1,3-dimethylphenylmagnesium bromide, and of a and f-naphthylmagnesium bromides, have prepared the corresponding aryltriethoxysilanes. Reactions with ethereal solutions of propylmagnesium bromide (Bibl.60), butyl- and amylmagnesium chloride (Bibl.61) have been similarly run.

Escers of orthosilicic acid containing alkoxy groups of relatively high molecular weight reacts only difficultly with organomagnesium compounds or do not react
at all, such as, for instance, phenylmagnesium bromide with tetra-p-tolyoxysilane (Bibl.62).

It is very important that not only tetraalkoxysilanes enter into reaction with organomagnesium compounds, but also, with no less intensity, their partial hydrolyzates as well. Thus, for example, the reaction of partially hydrolyzed tetraethoxy- silanes with ethyl bromide and magnesium leads to the formation of ethylethoxysil- anes and of ethylethoxysiloxanes, which, after hydrolysis and condensation, form polysiloxanes containing, on the average, not less than two ethyl radicals per sil- con atom (Bibl.63, 124).

Organic compounds of other metals likewise react with esters of orthosilicic acid to form substituted esters. But these reactions are not of such great practi- cal importance as the reactions with organomagnesium compounds.

The reaction with organolithium compounds proceeds smoothly and can easily be regulated (Bibl.125). Owing to the high cost of lithium, however, the practical importance of reactions of this type is small. By the aid of organolithium com- pounds, it is possible to substitute organic radicals for all four alkoxy groups in the molecule of an ester of orthosilicic acid; thus, tetraphenylsilane in 98% yield and tetrabutylsilane in 97% yield have been prepared from tetraethoxysilane (Bibl.64). Compounds with complex organic groups are easily prepared by alkylation or alkoxysilanes, using organolithium compounds. Thus, for example, the following compounds have been prepared (Bibl.65): n-(CH₃)₂NC₆H₄Si(OC₂H₅)₃; n-CH₃C₆H₄Si(OC₂H₅)₃; (o,n)-(CH₃)₂C₆H₃Si(OC₂H₅)₃; n-C₆H₄C₆H₄Si(OC₂H₅)₃; n-H₂NC₆H₄Si(OC₂H₅)₃; (HOCH₂C₆H₄)₂Si(OC₂H₅)₂ etc.

By the aid of organolithium compounds it has been possible to introduce three branched radicals into the tetraethoxysilane molecule (Bibl.66):

\[ \text{Si(OC}_2\text{H}_5)_4 + 3(\text{CH}_3)_2\text{C} \text{H} \text{Li} \rightarrow (\text{CH}_3)_2\text{C} \text{H}_3\text{SiOC}_2\text{H}_5 + 3\text{C}_8\text{H}_8\text{OLi} \]

When two different organolithium compounds act in succession on tetraethoxy-
silane, substituted esters with unlike radicals attached to the same silicon atom can be prepared; for instance methylphenyldiethoxysilane (Bibl.65, 66).

Under the action of metallic sodium on a mixture of tetraethoxysilane and alkyl halide, the alkoxy group is replaced by an organic radical:

\[
\text{Si(OR')}_4 + 2\text{Na} + \text{RX} \rightarrow \text{RSi(OR')}_3 + \text{NaX} + \text{NaOR'}
\]

In this way (Bibl.67) isoamyltrimethoxysilane mixed with diisooamyldiethoxysilane, in respective yields of 39% and 25% have been prepared, as well as phenyltrimethoxysilane, cyclohexyltriethoxysilane, and mono-, di-, and triethylethoxysilanes.

The reaction with organozinc compounds proceeds only at temperatures over 300°C, but in the presence of metallic sodium, tetramethoxysilanes and diethylzinc, for instance, react at the boiling point of the mixture to form ethyltrimethoxysilane (Bibl.68). On heating tetraethoxysilane with diethylzinc in a sealed tube, tetraethylsilane is formed (Bibl.69).

**Reaction with Acid Halides**

The processes of substitution of halogen atoms for alkoxy groups in the esters of orthosilicic acid proceed when the esters react with acid halides, and may be schematically represented as follows:

\[
\text{Si-OR} + R'X \rightarrow \text{Si-X} + \text{ROR'}
\]

where \( R \) = radical;

\( R' \) = acid residue (inorganic or organic);

\( X \) = halogen.

Depending on the activity of the acid halide, the reaction temperature, the molecular weight and structure of the alkoxy group, the number of alkoxy groups in the molecule, and the proportions of the reagents, halo-esters with varying numbers
of alkoxy groups, or \( \text{SiCl}_4 \), may be formed.

The reaction of tetraethoxysilane with phosphorus pentachloride was first studied by D.I. Mendeleyev (Bibl.2), who succeeded in replacing two ethoxy groups by chlorine atoms:

\[
\text{Si(OC}_2\text{H}_5)_4 + 2\text{PCl}_3 \rightarrow 2\text{POCl}_3 + 2\text{C}_2\text{H}_5\text{Cl} + (\text{C}_2\text{H}_5\text{O})_3\text{SiCl}_2
\]

Later Stokes (Bibl.70) found that when a mixture of these reagents was heated to 140°C, ethoxytrichlorosilane was the principle product. The last ethoxy group is more difficult to replace, \( \text{SiCl}_4 \) being formed in very small amounts.

When tetraethoxysilane reacts with phosphorus oxychloride (Bibl.71, 113) on heating the mixture for 2 hours to a temperature of 180 - 200°C, ethyl chloride and a mixed silicophosphoric oxychloride are formed:

\[
\text{Si(OC}_2\text{H}_5)_4 + 2\text{POCl}_3 \rightarrow \text{SiP}_2\text{OCl}_4 + 4\text{C}_2\text{H}_5\text{Cl}
\]

When this oxychloride reacts with phosphorus pentachloride, \( \text{SiCl}_4 \) is formed.

Tetraphenoxysilane reacts with phosphorus oxychloride to form \( \text{SiCl}_4 \) directly (Bibl.70):

\[
\text{Si(OC}_2\text{H}_5)_4 + 4\text{POCl}_3 \rightarrow \text{SiCl}_4 + 4\text{POCl}_3\text{OC}_2\text{H}_5
\]

The reaction proceeds quantitatively on heating the mixture for 16 hours at 240°C.

On action of fluorinating reagents on esters of orthosilicic acid, the alkoxy group is easily replaced by a fluorine atom:

\[
\text{Si(OC}_2\text{H}_5)_4 + \text{SbF}_3 \rightarrow \text{FSi(OC}_2\text{H}_5)_3 + \text{F}_3\text{SbOC}_2\text{H}_5
\]

The most convenient method for preparing alkoxyfluorosilanes is based on this reaction (Bibl.27):

On heating a mixture of 833 g of tetramethoxysilane, 477 g of antimony trifluoride, and 3 g of antimony pentachloride for 1½ hours, a mixture of 72 g of
diethoxydifluorosilane and 63 g of triethoxyfluorosilane is obtained. It has not been possible to isolate the ethoxytrifluorosilane, obviously owing to its pronounced tendency to the symmetrization reaction.

When esters of orthosilicic acids are heated with acetyl chloride or benzoyl chloride, the alkoxy group is replaced by a chlorine atom (Bibl.72):

\[
\text{Si(OC}_2\text{H}_3)_4 + RCOCl = \text{ClSi(OC}_2\text{H}_3)_3 + \text{RCOOC}_2\text{H}_5
\]

When equimolecular quantities of tetraethoxysilane and acetyl chloride react at 135°C, the yield of triethoxychlorosilane is 90%. Tetraethoxysilane, heated with 2 mols of acetyl chloride (Bibl.73) to 185°C, forms diethoxydichlorosilane in insignificant yield; when an excess of acetyl chloride (5 mols) is used, a certain amount of ethoxytrichlorosilane is formed. On prolonged heating of a mixture of tetraethoxysilane and acetyl chloride or benzoyl chloride at 200°C, SiCl₄ can be obtained (Bibl.70). Acetyl bromide and benzoyl bromide (Bibl.73) react with tetraethoxysilane at 185°C, but only ethyl bromide and ethyl acetate or ethyl benzoate have been isolated from among the individual reaction products in the mixture.

On heating a mixture of an ester of orthosilicic acid and SiCl₄ to above 160°C, a mixture of alkoxychlorosilanes is formed. The composition of the mixture depends on the proportion between the starting reagents. Both tetraalkoxysilanes (Bibl.74) and tetraaryloxysilanes (Bibl.13) enter into this reaction.

**Reaction with Aluminum Chloride**

In contrast to the halo-esters, the full esters of orthosilicic acid are not decomposed by small amounts of aluminum chloride, and in presence of a large excess of aluminum chloride, an aluminosilicate is formed (Bibl.75):

\[
6\text{Si(OR)}_4 + 2\text{AlCl}_3 = (\text{SiO})_3(\text{Al}_4\text{O}_5) + 6\text{RCl} + 9\text{R}_2\text{O}
\]

This reaction may be used to prepare simple ethers, for instance dibutyl ether. The higher tetraalkoxysiloxanes react with difficulty with aluminum chloride.
Reaction with Halogen Hydrides

The esters of orthosilicic acid display a varying stability to the action of gaseous hydrogen halides. The esters and haloesters hardly react at all with HCl, but react easily and almost quantitatively with HI. When tetraethoxysilane is heated with HCl in a bomb at 185°C, an insignificant amount of ethyl chloride is obtained. Tetraphenoxysilane reacts with HCl only at 300°C, forming phenol. HBr reacts partially with tetraalkoxysilanes on heating; forming alkyl bromide, alcohol and polysiloxane. Tetrabutoxyxilane, for instance, reacts with HBr, forming 20% of ethyl bromide and 2% of butanol. HI quantitatively decomposes tetraalkoxysilanes, forming the alkyl iodide, the alcohol, and polysiloxanes.

It is possible that the reaction of esters with a hydrogen halide may lead initially to the replacement of an alkoxy group by a halogen atom:

\[
\text{Si-OR + HX } \rightarrow \text{Si-X + ROH}
\]

If \(R\) is an aromatic radical, the reaction stops there, but an aliphatic alcohol reacts in turn, at a high temperature, with the hydrogen halide, forming the alkyl halide and water:

\[
\text{ROH + HX } = \text{RX + H}_2\text{O}
\]

which hydrolyzes the original ester to form polysiloxanes.

The Symmetrization Reaction

A characteristic property of mixed asymmetric esters and haloesters of orthosilicic acid, as it is in general for all monomeric organic derivatives of silicon, is their power on heating to rearrange to form molecules of symmetrical structure. Thus, butoxytrithoxysilane, on heating, undergoes the reaction:

\[
2(C_2H_5O)_3Si(C_C_6H_5)_3 = (C_2H_5O)_3Si(C_C_6H_5)_2 + Si(C_C_6H_5)_4
\]
Decomposition in a Hydrogen Atmosphere

Dolgov and Vol'nov (Bibl.76) have studied the reaction of cleavage of various esters of orthosilicic acid in a hydrogen atmosphere under 100 atm pressure. They found that the stability of the aliphatic esters under these conditions is greater, the lower the molecular weight of the radical. Thus, on heating tetraethoxysilane for 20 hours at 200°C, 20% of it is decomposed, forming hexaethoxydisilane:

\[
\text{Si(OC}_2\text{H}_4\text{)}_4 + \text{H}_2 = (\text{C}_2\text{H}_5\text{O})_3\text{SiSi(OC}_2\text{H}_3\text{)}_3 + 2\text{C}_2\text{H}_5\text{OH}
\]

Tetraallyloxysilane under these conditions decomposes to the extent of 57.5%. At higher temperatures the processes of pyrolysis take place, accompanied by the formation of water, silica, and polymeric unsaturated hydrocarbons.

The aryloxysilanes are more stable and decompose only when heated to 400°C, forming elementary silicon:

\[
\text{Si(OC}_4\text{H}_4\text{)}_4 + 2\text{H}_2 = \text{Si} + 4\text{C}_2\text{H}_5\text{OH}
\]

Reactions with Organic Acids, Aldehydes, and Ketones

Organic acids hydrolyze the esters of orthosilicic acids:

\[
\text{Si(OR)}_4 + 4\text{R}'\text{COOH} = [\text{Si(OH)}_4] + 4\text{R'}\text{COOR}
\]

When less than the theoretical amount of acid acts on esters, intermediate products of hydrolysis, polyalkoxysiloxanes, can be obtained.

On heating a mixture 208 g of tetraethoxysilane (Bibl.77) and 120 g of glacial acetic acid at boiling point for 1 hour, 46 g of a mixture of polyethoxysiloxanes passing over up to 135°C (at 2 mm) was obtained, together with a large amount of high-molecular nonvolatile products (a fuscous retort residue). When 0.5 mol of acetic acid per mol of tetraethoxysilane was used, the main product of the reaction is hexaethoxydisiloxane; when the reacting substances are taken in the molecular ratio of 1 : 1, the reaction yields a viscous mixture of soluble polymers of mole-

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cular weight ranging from 700 to 10,000, with an insignificant number (2.53 - 4.91%) of acetoxy groups.

The end product of the reaction is anhydrous, highly active, silica gel, without any electrolytes (Bibl.7).

Aldehydes and ketones, as well as chloral hydrate, are esterified on reaction with tetraalkoxysilanes, and the esters of orthosilicic acid are partially or completely hydrolyzed (Bibl.6):

\[ 3\text{Si(OCH}_3\text{)}_4 + \text{CH}_2\text{CHO} = \text{CH}_3\text{CH(OCH}_3\text{)}_2 + (\text{CH}_3\text{O})_2\text{SiOSi(OCH}_3\text{)}_4 \]
\[ 4\text{CH}_2\text{CCH(OH)}_2 + \text{Si(OC}_2\text{H}_4\text{)}_4 = 4\text{C}_3\text{H}_5\text{CCH(OH)}_2 + \text{Si(OH)}_4 \]

The process is conducted in alcohol (2 - 3 mols per mol of aldehyde or ketone and 1.1 mol of tetraethoxysilane). HCl (10 drops of a saturated alcohol solution) is used to catalyze the reaction. Dimethylacetal is obtained in the cold; while heating is necessary to complete the reaction of formation of the higher acetals. Polysiloxanes are decomposed by alkali; the mixture is washed and then rectified. The yield of acetals is 70 - 90% of theoretical.

**Reactions with Acid Anhydrides (Bibl.78)**

Under the action of acetic anhydride on tetraethoxysilane, acetyloethoxysilanes are formed:

\[ \text{Si(OC}_2\text{H}_4\text{)}_4 + \text{CH}_3\text{COOCCH}_3 = \text{CH}_3\text{COOSi(OC}_2\text{H}_4\text{)}_2 + \text{CH}_3\text{COOCCH}_3 \]
\[ \text{CH}_3\text{COOSi(OC}_2\text{H}_4\text{)}_2 + \text{CH}_3\text{COOCCH}_3 = (\text{CH}_3\text{COO})_2\text{Si(OC}_2\text{H}_4\text{)}_2 + \text{CH}_3\text{COOCCH}_3 \]

It is believed that such compounds are able to dissociate in a medium of acetic anhydride, which might explain the side reaction of the formation of polysiloxanes:

\[ \text{CH}_3\text{COOSi(OC}_2\text{H}_4\text{)}_2 \rightarrow \text{CH}_3\text{COOSi(OC}_2\text{H}_4\text{)}_2^+ + \text{CH}_3\text{COO}^- \]
\[ \text{CH}_3\text{COOSi(OC}_2\text{H}_4\text{)}_2 \rightarrow \text{CH}_3\text{CO}^+ + \text{OSi(OC}_2\text{H}_4\text{)}_2^- \]
\[ \text{CH}_3\text{COOSi(OC}_2\text{H}_4\text{)}_2^- + \text{OSi(OC}_2\text{H}_4\text{)}_2^- \rightarrow \text{CH}_3\text{CO(OSi(OC}_2\text{H}_4\text{)}_2)\text{SiOC}_2\text{H}_4, n = 1, 2, \ldots \]
In the reaction with phthalic anhydride (Bibl.79), the reaction leading to the formation of polysiloxanes becomes the main reaction. 

\[ xC_6H_4(CO)O + xSi(OSiH_3)_4 = xC_6H_4(COOC_6H_5)_2 + [Si(OSiH_3)_2]_x \]

The process is conducted by heating an equimolecular mixture of these substances for 6 hours at 160°C.

**Reaction with Aromatic Hydrocarbons**

Tetraalkoxysilanes, as well as the ordinary mixed anhydrides of orthosilicic acid \( Si(OCOR)_4 \), react with aromatic hydrocarbons in the presence of aluminum chloride:

\[ Si(OR)_4 + 4C_6H_6 \overset{AlCl_3}{\longrightarrow} 4C_6H_5R + Si(OH)_4 \]

Petrov and Itkina (Bibl.72) have described a reaction between silicobutyric anhydride and aromatic hydrocarbons:

\[ Si(OCOCH_3)_4 + 4C_6H_6 = 4C_6H_5COC_6H_5 + Si(OH)_4 \]

Petrov (Bibl.80) conducted a number of analogous reactions with silicoformic anhydride, obtaining phenylformate:

\[ Si(OCOH)_4 + 4HOC_6H_5 = 4C_6H_5CHO + Si(OH)_4 \]

tolyl formate

\[ Si(OCHO)_4 + HOC_6H_4CH_3 = 4CH_3C_6H_4CHO + Si(OH)_4 \]

and p-tolylaldehyde

\[ Si(OCHO)_4 + 4C_6H_5CH = 4CH_2C_6H_4CHO + Si(OH)_4 \]

Petrov and Lagacheva (Bibl.81) prepared a number of aromatic ketones in high yield.
yield. We give the method of preparing tolylphenylketone.

A mixture of 31 g of benzoic acid, 42.5 g of SiCl₄ and 200 ml of toluene is heated on the water bath and is held over the boiling bath until the evolution of HCl stops. After the mixture has cooled, 45 g of aluminum chloride is introduced into it (while the reaction mass is allowed to cool on the water bath). The water bath is gradually heated to boiling; the reaction mass is held there until the evolution of HCl stops, and is then cooled, poured on ice, and extracted with ether; the ethereal solution is dried and distilled. The mixture of o- and p-tolylphenylketones, in 86% total yield, can be separated by fractional crystallization.

Other ketones were prepared by a similar method. The yields of benzophenone was 58%, of methylchlorophenylketone 45.4%, of methytolylketone 62.7%, and of acetophenone 47%.

The simple tetraalkoxysilanes react similarly with aromatic hydrocarbons in the presence of aluminum chloride. Thus, for example, tetraethoxysilane and benzene form a mixture of various ethylbencenes up to hexaethylbensene (Bibl.7).

The Polymerisation Reaction

The unsaturated esters of orthosilicic acids, for example tetraallyloxysilane and tetramethallyloxysilane, are able to polymerise at the double bonds, forming insoluble polymers that do not melt at temperatures up to 300°C. The process of polymerisation at 250°C lasts 40 hours, but under the same conditions, but with the addition of 0.5% of bensoyl peroxide, it takes only 25 hours.

Properties of Alkoxysilanes Containing the Si-H Bond, and of Alkoxydisilanes

Alkoxysilanes of the composition H₂Si(OR)₄-x combine the properties of silanes and esters of orthosilicic acid. Like the corresponding silanes, the alkoxysilanes very readily oxidise, react with halogens to form halo-esters, but are considerably more stable than the silanes. Trialkoxysilanes H₂Si(OR)₃ are the principal such compounds that have been studied and described. The hydrolysis of trialkoxysilanes in
a neutral, acid, or weakly alkaline medium, and the condensation of the hydrolysis
products, proceeds by a reaction similar to that of the hydrolysis of
mono-substituted esters of orthosilicic acid, namely, the -Si-H bond is preserved
during the process of hydrolysis, and the end product of condensation has the
formula \((\text{HSiO}_1.5)_x\).

When esters or the products of their hydrolysis react with alkalies (Bibl.83),
1 mol of hydrogen for each -Si-H bond is evolved.

The products of esterification of hexachlorodisilane are likewise analogs of
the tetraalkoxysilanes in their properties. Their hydrolysis usually takes place
with the -Si-Si- bond being preserved, but in an alkaline medium this bond is
broken, and 1 mol of hydrogen is evolved for each -Si-Si- bond (Bibl.83):

\[-\text{Si-Si} + 2\text{KOH} = 2\text{SiOK} + \text{H}_2\]

**HALOESTERS OF ORTHOSILICIC ACID**

Haloesters are reactive organosilicon compounds combining the properties of the
esters of orthosilicic acid with those of halogen derivatives. Mixed esters of
orthosilicic acid and esters of polysilicic acid can be obtained easily and in good
yield from the haloesters.

The individual mono-, di-, and tri-substituted esters of orthosilicic acid can
also be easily prepared by the aid of the haloesters.

**Methods of Preparation**

The most widely used method of preparing the haloesters of orthosilicic acid is
the reaction of SiCl\(_4\) with alcohols or phenols, taken in an amount insufficient for
complete esterification:
The reaction for the preparation of haloesters also takes place very easily, and for the lower aliphatic alcohols proceeds practically to completion, at room temperature.

Kalinin (Bibl.84) has established that the most convenient method of preparing chloro-esters is the reaction between solutions of SiCl₄ and the alcohol (1 : 1) in an inert solvent, for instance benzene. The process is conducted by pouring a solution of the alcohol in benzene (1 : 1) into a solution of SiCl₄ in benzene (1 : 1) with stirring; in this case the SiCl₄ will be in excess, and the quantity of total esters of orthosilicic acid formed will be minimum. The mixture is heated 50 - 60℃ until the evolution of HCl ceases; the benzene (about 96%) is distilled off, and the mixture is then distilled in vacuo. It is advisable to aspirate dry air through the reaction mixture in order best to remove the HCl during the process of synthesis. In this way the following were synthesized: triethoxychlorosilane (in 56.9% yield), triisobutoxychlorosilane (in 52.2% yield), and triisooamyloxychlorosilane (in 56% yield).

**Preparation of allyloxychlorosilanes (Bibl.12).** In a three-liter flask, provided with a stirrer, a dropping funnel, and a gas-discharge tube, 612 g of SiCl₄ are placed. Under cooling, over a period of 2½ hours, 523 g of allyl alcohol is added, and the mixture is transferred to a retort and rapidly heated. The alcohol is distilled off together with the HCl.

Rectification of the residue at 32 ℃ yields 6.1 g of allyloxytrichlorosilane; 130 g of diallyloxydichlorosilane; 44.9 g of triallyloxychlorosilane, and 112 g of tetraallyloxyxilane.

To increase the yield of diallyloxydichlorosilane, 1.8 mol of allyl alcohol per
mol of SiCl₄ should be taken, while to prepare allyloxytrichlorosilane, 1.1 mol of this alcohol should be taken instead.

Butoxychlorosilanes have been prepared by the action of butylalcohol on SiCl₄ (Bibl.85).

Tertiary butoxy- and amyloxy silanes (Bibl.86), as well as several mixed alkoxy-butoxychlorosilanes have been prepared by esterification of SiCl₄ or chloroester by tertiary butyl or amyl alcohol in the presence of pyridine, to neutralize the HCl formed. When the mixed haloesters are prepared by partial esterification of the haloesters, the process is as a rule conducted in the presence of organic bases; otherwise the HCl formed will encourage the reaction of redistribution of the alkoxy groups, and, instead of the desired product, a large number of compounds, whose separation is almost impossible, are usually obtained.

Preparation of ethoxyallyloxydichlorosilane (Bibl.12). A solution of 1 mol of allyl alcohol in 150 ml of benzene is added under stirring to a cooled mixture consisting of 1 mol of ethoxytrichlorosilane, 1.3 mol of isoquinoline, and 200 ml of benzene. The mixture is heated to precipitate the isoquinoline hydrochloride. The precipitate is filtered off, and the filtrate is rectified under reduced pressure.

It is interesting to note that the cyclohexyloxy group is obviously attached rather firmly to the silicon atom and does not enter into the redistribution reaction, so that the mixed halo-esters can be prepared from cyclohexanol without the use of neutralizing agents. Thus (Bibl.12), allyloxytrichlorosilane and an equimolecular quantity of cyclohexanol yield 50% of allyloxy-cyclohexyloxydichlorosilane and 13% of allyloxydicyclohexyloxychlorosilane.

Vol'nov (Bibl.87) has prepared all three alkoxychloro-esters from n-hexyl and n-octyl alcohols with SiCl₄.

Preparation of hexyloxy- and octyloxychlorosilanes. Hexyloxychlorosilane was prepared by reacting 30 g of hexylalcohol and 60 ml of SiCl₄ in the cold. The yield was 72%. Dihexyloxydichlorosilane was similarly prepared from 44 g of the
alcohol and 34 g of SiCl₄. It is considerably more difficult to prepare trihexyl-
oloxysilane. A 34 g portion of SiCl₄ was cooled to a temperature of -10°C, and, under stirring, 166 g of hexyl alcohol was added at a rate of 1 drop every 2 sec. The mixture was heated 1 - 2 hours on a water bath and then distilled under 10 mm Hg. Tetrahexyloxysilane was the main reaction product. The trihexyloxysilane was separated only on repeated rectification (165 - 168°C at 5 mm).

By briefly heating a mixture of 55 g of SiCl₄ and 30 g of octyl alcohol on a boiling water bath, octyloxycyclicosilane in 60% yield was prepared; from 17 g of SiCl₄ and 28 g of the alcohol, a mixture containing 28% of dioctyloxidichlorosilane and 22% of trioxylxychlorosilane was obtained.

The preparation of the chloro-esters of the higher aliphatic alcohol likewise involves no difficulty.

**Preparation of dodecyloxysilanes.** To dodecyl alcohol a solution of SiCl₄ in petroleum ether is added under stirring and cooling to -5°C (Bibl.88). The mixture is heated to remove the HCl and is distilled under a residual pressure of 5 mm; on the action of an excess of SiCl₄ on dodecyl alcohol, the main reaction product is dodecyloxysilane; but if 2 - 3 mols of alcohol are taken for every mol of SiCl₄, then di- and tridodecyloxysilanes are principally formed.

Vol'nov (Bibl.89) has prepared all three chloro-esters of the structure 

\[ [(CH₂Cl)₂CHO]ₓSiCl₄₋ₓ \]  (where \( x = 1, 2, \) and 3), as well as the haloesters 

\( (BrCH₂CH₃CH₂O)ₓ \)  (where \( x = 1 \) and 2), by reacting SiCl₄ with halohydrins of glycerol.

All three phenoxychlorosilanes (Bibl.90) may be prepared when a mixture of SiCl₄ with 2 mols of phenol is heated to 100°C until the evolution of HCl stops, but the best yield is obtained (Bibl.91) when the reaction is run at 200°C.

**Preparation of phenoxychlorosilanes.** A solution of 2.25 mols of phenol in an equal volume of benzene is added to an equimolecular quantity of SiCl₄; the mixture is stirred until the evolution of HCl stops, then heated to 200°C and held at that
temperature 3 to 4 hours. Distillation at 60 mm Hg yields 20% of phenoxytrichlorosilane, 35 - 40% of diphenoxydichlorosilane, 35% of triphenoxychlorosilane, and 2 - 5% of tetraphenosilane.

Tri-(p-bromophenoxy)-chlorosilane has been prepared by a similar method from p-bromophenol.

Vol'nov and Mishelevich (Bibl.92) reacted SiCl₄ with thymol, guaiacol, and carvacrol, and obtained all the possible chloroesters. The reaction was completed on heating the mixture over the water bath for 10 - 20 minutes.

On the reaction of SiCl₄ with menthol (Bibl.93), menthoxchlorosilanes were prepared.

The fluoro-esters of orthosilicic acid may be prepared by esterification of the fluorochlorosilanes; in this case the -Si-F bond is completely preserved.

As a result of the reaction of 30 g of difluorodichlorosilane with 37.8 g of butyl alcohol dissolved in 35 g of ether at -78°C, 17.5 g of dibutoxydifluorosilane are obtained (Bibl.94). Another widespread method of preparing haloesters of orthosilicic acid is based on the reaction of substitution of halogen atoms for alkoxy groups of a full ester.

The reaction between esters of orthosilicic acid and fluorinating reagents is of the most importance for practical purposes, since this is a convenient method of preparing fluoro-esters of orthosilicic acid.

The stability of the -Si-F bonds (especially in trialkoxyfluorosilanes) is so great, that under the action of an alcohol, the fluorine is not replaced by an alkoxy group, but alcoholysis of the alkoxyfluorosilanes takes place instead:

\[ \text{FSi(OC}_2\text{H}_5)_3 + 3\text{C}_2\text{H}_5\text{OH} = \text{FSi(OC}_4\text{H}_9)_3 + 3\text{C}_2\text{H}_5\text{OH} \]

A mixture of 36.4 g of triethoxyfluorosilane and 53.9 g of butyl alcohol is
Table 37

<table>
<thead>
<tr>
<th>Physical Properties of Aliphatic Haloesters of Orthosilicic Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>a)</strong> Name; <strong>b)</strong> Formula; <strong>c)</strong> Boiling Point, °C; <strong>d)</strong> Specific Gravity, d</td>
</tr>
<tr>
<td>Methoxytrichlorosilane</td>
</tr>
<tr>
<td>Dimethoxychlorosilane</td>
</tr>
<tr>
<td>Trimethoxychlorosilane</td>
</tr>
<tr>
<td>Ethoxytrichlorosilane</td>
</tr>
<tr>
<td>Triethoxychlorosilane</td>
</tr>
<tr>
<td>Ditributylammonium dichlorosilane</td>
</tr>
<tr>
<td>Triallyloxychlorosilane</td>
</tr>
<tr>
<td>Tripropoxychlorosilane</td>
</tr>
<tr>
<td>Tri(dimethylamino)silane</td>
</tr>
<tr>
<td>Di-(ethoxy)-allyloxytrichlorosilane</td>
</tr>
<tr>
<td>Di-(O'-dichloroiso-propoxy) - dichlorosilane</td>
</tr>
<tr>
<td>Tri-(O₃P'-difenyl)-chlorosilane</td>
</tr>
<tr>
<td>Triethyltoxytrichlorosilane</td>
</tr>
<tr>
<td>Ethoxytrifluorosilane</td>
</tr>
<tr>
<td>Tris(trifluoromethyl)silane</td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Boiling Point, °C; d) Specific Gravity, d; e) Bibliography
### Table 38

**Physical Properties of Aromatic, Aliphatic-aromatic and Alicyclic-chloro-Esters of Orthosilicic Acid**

<table>
<thead>
<tr>
<th>a) Name</th>
<th>b) Formula</th>
<th>c) Boiling Point, °C</th>
<th>d) Specific Gravity, $d_2^20$</th>
<th>e) Refractive Index, $n_D^{15}$</th>
<th>f) Bibliography</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenoxytrichlorosilane</td>
<td>$C_6H_5OSiCl_3$</td>
<td>104-150</td>
<td>-</td>
<td>-</td>
<td>90, 91</td>
</tr>
<tr>
<td>Triphenoxydichlorosilane</td>
<td>$(C_6H_6)_2SiCl_2$</td>
<td>(13 mm)</td>
<td>183-186</td>
<td>-</td>
<td>90, 91</td>
</tr>
<tr>
<td></td>
<td>$(C_6H_6)_2SiCl_2$</td>
<td>(60 mm)</td>
<td>167-171</td>
<td>-</td>
<td>90, 91</td>
</tr>
<tr>
<td></td>
<td>$(C_6H_6)_2SiCl_2$</td>
<td>(13 mm)</td>
<td>215-218</td>
<td>-</td>
<td>90, 91</td>
</tr>
<tr>
<td></td>
<td>$(C_6H_6)_2SiCl_2$</td>
<td>(60 mm)</td>
<td>220-230</td>
<td>-</td>
<td>90, 91</td>
</tr>
<tr>
<td></td>
<td>$(C_6H_6)_2SiCl_2$</td>
<td>(14 mm)</td>
<td>242-256</td>
<td>-</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>$(C_6H_6)_2SiCl_2$</td>
<td>(65 mm)</td>
<td>122-134</td>
<td>1.3462</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>$(C_6H_6)_2SiCl_2$</td>
<td>(23 mm)</td>
<td>198-200</td>
<td>1.1250</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>$(C_6H_6)_2SiCl_2$</td>
<td>(3 mm)</td>
<td>231-235</td>
<td>1.0867</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>$(C_6H_6)_2SiCl_2$</td>
<td>(7-8 mm)</td>
<td>108-111</td>
<td>1.1798</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>$(C_6H_6)_2SiCl_2$</td>
<td>(4 mm)</td>
<td>134-136</td>
<td>1.3677 (18°)</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>$(C_6H_6)_2SiCl_2$</td>
<td>(30 mm)</td>
<td>140-148</td>
<td>1.885 (25°)</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>$(C_6H_6)_2SiCl_2$</td>
<td>(10 mm)</td>
<td>203-250</td>
<td>-</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>$(C_6H_6)_2SiCl_2$</td>
<td>(10 mm)</td>
<td>215</td>
<td>-</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>$(C_6H_6)_2SiCl_2$</td>
<td>(10 mm)</td>
<td>112</td>
<td>1.1430</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td>$(C_6H_6)_2SiCl_2$</td>
<td>(113 mm)</td>
<td>193</td>
<td>1.0380</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td>$(C_6H_6)_2SiCl_2$</td>
<td>(18 mm)</td>
<td>224-245</td>
<td>0.9784 (18.5)</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td>$(C_6H_6)_2SiCl_2$</td>
<td>(10 mm)</td>
<td>310-320</td>
<td>-</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>$(C_6H_6)_2SiCl_2$</td>
<td>(12 mm)</td>
<td>261</td>
<td>1.490</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>$(C_6H_6)_2SiCl_2$</td>
<td>(12 mm)</td>
<td>267</td>
<td>-</td>
<td>92</td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Boiling Point, °C; d) Specific Gravity, $d_2^20$; e) Refractive Index, $n_D^{15}$; f) Bibliography

Heated in a flask, used as the retort for a rectification column; the ethyl alcohol formed during the reaction is distilled off in 1 hour, while the residue is fractionated, boiling point 134 - 134.5°C at 32 mm. The yield of tributoxyfluorosilane is 59%.
Triallyloxyfluorosilane is obtained similarly from triethoxyfluorosilane and allyl alcohol, distilling off the ethyl alcohol during the course of 21/2 hours. The yield is 49%.

Physical Properties

The halo-esters of orthosilicic acid are colorless liquids with a sharp odor recalling that of SiCl₄. They are readily soluble in inert organic solvents, and are rapidly hydrolyzed in air. They burn with a bright flame with a green border. They can be distilled without decomposition. The vapor of some of the lower chloro-esters, when mixed with air, take fire with an explosion.

Table 37 (page 304) gives the principal physical properties of the aliphatic haloesters of orthosilicic acid. Table 38 (page 305) gives the properties of aromatic, aliphato-aromatic and alicyclic chloro-esters of orthosilicic acid. Table 39 gives the properties of mixed chloroesters of orthosilicic acid.

Table 39

Boiling Points of Mixed Chloroesters of Orthosilicic Acid

<table>
<thead>
<tr>
<th>a) Name</th>
<th>b) Formula</th>
<th>c) Boiling Point, °C</th>
<th>d) Bibliography</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methoxy- (ethoxy) -(butoxy)-</td>
<td>(CH₃O)(CH₃O)(CH₃O)SiCl</td>
<td>159-160</td>
<td></td>
</tr>
<tr>
<td>chlorosilane</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethoxy- (allyloxy)- chlorosilane</td>
<td>(C₂H₅O)CH₂=CHCH₂OSiCl</td>
<td>85-86 (32 mm)</td>
<td></td>
</tr>
<tr>
<td>Phenoxy- (methoxy)-(ethoxy)-</td>
<td>(CH₃O)(CH₃O)C₆H₄OSiCl</td>
<td>244</td>
<td></td>
</tr>
<tr>
<td>chlorosilane</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethoxy- (allyloxy)- chlorosilane</td>
<td>(CH₂=CHCH₂O)(C₆H₄O)SiCl</td>
<td>143-144 (32 mm)</td>
<td></td>
</tr>
<tr>
<td>Allyloxydi- (cyclohexyl-</td>
<td>(CH₂=CHCH₂O)(C₆H₄O)SiCl</td>
<td>148 (5 mm)</td>
<td></td>
</tr>
<tr>
<td>oxy)- chlorosilane</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethoxy- (allyloxy)- chlorosilane</td>
<td>(CH₂=CHCH₂O)SiCl</td>
<td>128</td>
<td></td>
</tr>
<tr>
<td>Phenoxo- (phenoxy)- chlorosilane</td>
<td>(CH₃O)(CH₂=CHCH₂OSiCl)</td>
<td>140 (32 mm)</td>
<td></td>
</tr>
<tr>
<td>Cyclicloxy-(allyloxy)- chlorosilane</td>
<td>(CH₂=CHCH₂O)SiCl</td>
<td>216 (752 mm)</td>
<td></td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Boiling Point, °C; d) Bibliography
Chemical Properties

Hydrolysis

The haloesters of orthosilicic acid are hydrolyzed and condensed by the same reactions as the esters of orthosilicic acid, but the rate of hydrolysis of the haloesters is considerably higher (approximately of the same order as that of the hydrolysis of the tetrahalosilane). The hydrogen halide formed during the first stage of hydrolysis evidently catalyzes the process of hydrolysis of the alkoxy groups. The most active catalyst among the halogen hydrides is HF; thus the hydrolysis of alkoxychlorosilane by water at room temperatures proceeds slowly and leads to the formation of a transparent solution, while the hydrolysis of the alkoxyfluorosilanes (Bibl.27) is practically instantaneous, and leads to the formation of silica gel. The liberation of halogen hydride, likewise, apparently encourages the processes of rearrangement of the ether bonds. Thus, for instance, when dialkoxydichlorosilanes are treated with water, tetraalkoxysilane is formed (Bibl.12):

\[ 2(RO)\text{SiCl}_2 + H_2O = Si(OH)_4 + Si(OR)_4 + 4HCl \]

The processes of hydrolysis of alkoxychlorosilanes proceeds somewhat differently in the presence of organic basis (quinoline or pyridine) which neutralize the HCl. In this case, as a rule, no cleavage of the alkoxy group takes place and the reaction proceeds, forming alkoxydisiloxanes. The hydrolysis of trialkoxychlorosilanes leads to the formation of the alkoxydisiloxane:

\[ 2(C_2H_5_\text{O})_3\text{SiCl} + H_2O + 2C_2H_5H \rightarrow (C_2H_5_\text{O})_2\text{SiOSi(OC}_2H_5)_2 + 2C_2H_5N.HCl \]

Hydrolysis of triethoxychlorosilane. To a mixture of 19.9 g of triethoxychlorosilane and 12 g of pyridine, 20 ml of water is added. The water layer is then separated, and the product is washed with several portions of a 15% aqueous solution of sodium chloride and is dried 18 hours over calcined calcium chloride.
Distillation of the mixture in vacuo (at 3 mm) yields 10.2 g of hexasthoxysiloxane (Bibl.12) (60% of theoretical).

The hydrolysis of mixed trialkoxychlorosilanes, for instance of diethoxyallyloxychlorosilane, leads to the formation of the corresponding mixed disiloxanes:

\[
2(C_2H_5O)CH=CH-CH_2OSiCl + H_2O + 2C_2H_4N \rightarrow (C_2H_5O)2(C_2H_4O)SiOSi(OC_2H_5)(OC_2H_5)C_2 + 2C_2H_4N\cdot HCl
\]

On hydrolysis of dialkoxydichlorosilanes and of alkoxytrichlorosilanes in the presence of bases, polyalkoxysilanes, which in some properties recall polyalkylsiloxanes, are obtained.

\[
x(C_2H_5O)_2SiCl_2 + xH_2O + 2xC_2H_4N \rightarrow [(C_2H_5O)_2Si(U)]_x + 2xC_2H_4N\cdot HCl
\]

**Hydrolysis of dibutoxydichlorosilane (Bibl.37).** To a solution of 0.2 mols of dibutoxydichlorosilane in 200 - 300 g of benzene or dioxane, a mixture of 0.2 mols of water, 0.4 mol of pyridine, and 200 - 300 g of benzene is added. The reaction mixture is heated under a reflex condenser provided with a calcium chloride tube for 18 hours (the access of atmospheric moisture to the mixture must be prevented). After cooling, the pyridine hydrochloride is filtered off, and the mixture is rectified, gradually raising the temperature in the retort of the column to 400 - 500°C.

The polybutoxysiloxanes so prepared consist of the series of cyclical compounds \([Si(OC_4H_9)2]_x\) from cyclotrisiloxane

\[
\begin{align*}
\text{Si(OC}_4\text{H}_9)_2 & \\
\text{(C}_4\text{H}_9\text{O})_2\text{Si} & \\
\text{Si(OC}_4\text{H}_9)_2 & \\
\end{align*}
\]

to cyclooctasiloxane. The residue in the retort (a gel) amounts to only about 3% of the total amount of the hydrolysis products. The hydrolytic stability of cyclic compounds varies strongly, depending on the number of silicon atoms in the ring.
Thus, the cyclical hexamer is hydrolyzed only to the extent of 3% in 48 hours by boiling water, the pentamer 5%, while the trimer is 92% hydrolyzed (tetrabutoxysilane and hexabutoxydisiloxane are 5% hydrolyzed in 72 hours).

Acids exert a catalytic action on the process of hydrolysis and cause rapid coagulation of the mixture. Treatment of the cyclic polymers with sodium ethylate leads to rearrangement of the siloxane bonds and the formation of tetrabutoxysilanes.

A resinous polymer was obtained on the hydrolysis of dibutoxydichlorosilane in a solution of benzene and pyridine by ice water. The product so obtained contains somewhat more, on the average, than one butoxy group per silicon atom, and when heated to 360°C (at 3 mm) no volatile substances are separated from it. At 475°C, under 2 mm pressure, the formation of gas still does not occur. The decomposition of the film obtained on the basis of such a polymer begins only at a temperature of 575°C. In air, these films persist without hydrolysis for several weeks.

All alkoxyfluorosilanes immediately form gels on reacting with cold water. When they react with dry pyridine, dense (nongelatinous) products are obtained, which are rapidly hydrolyzed by water to form gels. The alkoxyfluorosilanes differ strongly from the corresponding alkoxychlorosilanes in their very high degree of decomposition under the action of water. This difference in the behavior of the alkoxyfluorosilanes and the alkoxychlorosilanes may be explained by the fact that the HF formed during hydrolysis acts as a catalyst considerably stronger than HCl for the reactions of hydrolysis and condensation of the alkoxy group. The fact that in the presence of pyridine, which accepts hydrogen fluoride, the reaction between triethoxyfluorosilane and butyl alcohol does not take place, while without pyridine the process of cleavage of the ethoxy groups and their replacement by butoxy groups proceeds rather rapidly, is also in agreement with this hypothesis.
Alkylation of Organometallic Compounds

Under the action of organometallic compounds on haloesters of orthosilicic acid, the halogen is replaced by an organic radical, forming substituted esters of orthosilicic acid. Kalinin, acting on trialkoxychlorosilanes with organomagnesium compounds, obtained a number of substituted esters of orthosilicic acid.

\[ \text{RMgX} + \text{SiCl}((\text{OR})_3) \rightarrow \text{RSi}((\text{OR})_3) + \text{MgXCl} \]
\( (R = \text{C}_2\text{H}_5 \ or \ \text{C}_8\text{H}_{15}; \ R' = \text{C}_2\text{H}_5; \ (\text{CH}_3)_2\text{CHCH}_2 \ or \ (\text{CH}_3)_2\text{CHCH}_2\text{CH}_2) \)

Phenylphenoxy silanes may be similarly prepared (Bibl.94):

\[ \text{Cl}_2\text{Si}((\text{OC}_6\text{H}_{13})_2 + 2\text{C}_6\text{H}_5\text{MgBr} = (\text{C}_6\text{H}_{13})_2\text{Si}((\text{OC}_6\text{H}_{13})_2) + 2\text{MgClBr} \]

The reaction between a haloester and sodium is of great practical interest, since the alkoxy groups enter into an alkylation reaction considerably more slowly than a halogen, and owing to this it is possible to obtain as a result of a reaction alkylalkoxy silanes with a predetermined number of \(-\text{Si-C} \) bonds:

\[ \text{Cl}_4\text{Si}((\text{OR})_2 + 4\text{Na} + 2\text{R'}\text{Cl} = \text{R'}\text{Si}((\text{OR})_2 + 4\text{NaCl} \]
\[ \text{ClSi}((\text{OR})_2 + 2\text{Na} + \text{R'}\text{Cl} = \text{R'}\text{Si}((\text{OR})_2 + 2\text{NaCl} \]

**Preparation of phenyltricyclohexyloxysiloxane** (Bibl.96). A mixture of tricyclohexyloxysilicon and chlorobenzene, under stirring, is added to a mixture of metallic sodium and ethyl ether. In 15 to 20 minutes, exothermic reaction begins. On the completion of the exothermic stage of the reaction, the flask is heated 5 hours on the water bath, the precipitate is filtered off, and the filtrate is distilled and rectified. The yield of phenyltricyclohexyloxysiloxane is 80% of theoretical.

Under the action of metallic sodium on phenoxychlorosilanes, the silicon is partially reduced to the elementary state, and tetraphenoxy silane is formed. The process is completed after a xylene solution of phenoxychlorosilanes is shaken with...
metalic sodium for 15 hours (Bibl.91).

\[ 4Cl_2SiOC_2H_5 + 12Na = Si(OOC_2H_5)_4 + 12NaCl + 3Si \]
\[ 2Cl_2Si(OC_2H_5)_2 + 4Na = Si(OOC_2H_5)_4 + 4NaCl + Si \]
\[ 4ClSi(OC_2H_5)_2 + 4Na = 3Si(OOC_2H_5)_4 + 4NaCl + Si \]

Thermal Transformation (Symmetrisation)

The principal factor determining the thermal stability of haloesters is their molecular structure, that is, their symmetry. The dialkoxydihalosilanes are stable compounds. The heating of diethoxydichlorosilane at the boiling point for 118 hours produces no changes in the product (Bibl.12). The asymmetrical haloesters undergo the reaction of symmetrisation on heating. Vol'nov (Bibl.97) studying the behavior of various haloesters of orthosilicic acids on heating, found that the alkoxytrichlorosilanes undergo rearrangement (symmetrisation) according to the reaction:

\[ 2(RO)SiCl_2 \rightarrow (RO)SiCl_4 + SiCl_4 \]

Ethoxytrichlorosilanes at 100°C is 25% rearranged in 2 hours, while it is quantitatively rearranged according to the reaction we have just given after 4 hours of heating at the boiling point, and a certain amount of ethyl chloride is also liberated. Hexoxytrichlorosilane is 6 - 13% rearranged on heating 4 hours at 100°C; phenoxytrichlorosilane on heating to 104 - 105°C for 5 hours is only 2 - 3% rearranged; thymoxytrichlorosilane begins to rearrange only at 126 - 136°C; while octoxytrichlorosilane only begins to rearrange on heating to boiling (234°C) for 6 hours. On heating guaiaciloxytrichlorosilane, in addition to the reaction given above, the following also takes place:

\[ -OCH_3 \rightarrow -OSiCl_3 \rightarrow -OSiCl_2 + CH_3Cl \]

The thermal rearrangement of trialkoxychlorosilanes proceeds according to the...
following general reaction:

\[ 2(RO)_2SiCl \rightarrow Si(OR)_4 + (RO)SiCl_2 \]

When heated 2 hours to 100°C, triethoxychlorosilane is 7 - 10% rearranged. On heating to boiling (160°C) for 6 - 7 hours, rearrangement is complete, and a certain quantity of ethyl chloride is also formed. Trioctyloxychlorosilane and triphenoxy-chlorosilane are modified only slightly at 100°C for 6 hours. In the latter case, traces of SiCl₄ are also formed.

**Reaction with Phosphorus oxychloride, Ammonia, and Amines**

Haloesters do not react with phosphorus oxychloride on heating to 175°C. When a mixture of phosphorus oxychloride and ethoxychlorosilane is heated in a sealed tube to 180 - 200°C, the following reaction takes place:

\[ GL_{2x}Si(OC₂H₅)₄ + POCl₃ \rightarrow SiCl₄ + SiP₂(OC₂H₅)₂ + C₂H₅Cl \]

When haloesters react with ammonia, alkoxyaminosilanes are formed, for example (Bibl.86):

\[ (C₆H₅O)₃SiCl₃ + 4NH₃ = (C₆H₅O)₂Si(NH₂)₂ + 2NH₄Cl \]

Amines react similarly with haloesters; forming alkoxy-substituted aminosilanes (Bibl.96):

\[ (C₆H₅O)(C₄H₉O)(CH₂O)SiCl + 2NH₄C₁₀H₅ \rightarrow (C₆H₅O)(C₄H₉O)(CH₂O)SiNH₂C₆H₄ + C₆H₄NH₂·HCl \]

**Reaction with Aluminum Chloride**

Haloesters of orthosilicic acid react actively with aluminum chloride, splitting off alkyl chlorides, only catalytic quantities of aluminum chloride being sufficient for the decomposition of the haloesters. Stokes (Bibl.75) who studied
In this process in detail, gives the following mechanism of reaction for ethoxychlorosilane:

\[
\begin{align*}
\text{Cl}_3\text{Si}(\text{OC}_2\text{H}_5)_3 + \text{AlCl}_3 & \rightarrow \text{SiO}_2 + \text{C}_4\text{H}_5\text{Cl} + (\text{C}_2\text{H}_5)_2\text{O} + \text{AlCl}_3 \\
n\text{Cl}_3\text{SiOC}_2\text{H}_5 + n\text{AlCl}_3 & \rightarrow (\text{SiOCR}_n) + n\text{C}_2\text{H}_5\text{Cl} + n\text{AlCl}_3 \\
\text{Cl}_2\text{Si}(\text{OC}_2\text{H}_5)_2 + \text{AlCl}_3 & \rightarrow \text{SiO}_2 + 2\text{C}_2\text{H}_5\text{Cl} + \text{AlCl}_3
\end{align*}
\]

On the basis of the hypothesis first expressed by Mendeleyev (Bibl.99) that oxygen compounds of silicon tend to form polysiloxanes, Stokes correctly postulates that the compound \((\text{SiOCR}_n)\) is not by any means a monomer, but is a complicated complex of polychlorosiloxanes. He postulates the following mechanism of their formation:

\[
\begin{align*}
\text{Cl}_3\text{SiOC}_2\text{H}_5 + \text{AlCl}_3 &= \text{Cl}_3\text{SiOAICl}_3 + \text{C}_2\text{H}_5\text{Cl} \\
\text{Cl}_3\text{SiOAICl}_3 + \text{C}_2\text{H}_5\text{OSiCl}_3 &= \text{Cl}_3\text{SiOSiCl}_3(\text{OC}_2\text{H}_5) + \text{AlCl}_3 \\
\text{Cl}_2\text{SiOSiOCl}_3(\text{OC}_2\text{H}_5) + \text{AlCl}_3 &= \text{Cl}_2\text{SiOSiCl}_3(\text{OAICl}_3) + \text{C}_2\text{H}_5\text{Cl} \\
\text{Cl}_2\text{SiOSiCl}_3(\text{OAICl}_3) + \text{C}_2\text{H}_5\text{OSiCl}_3 &= \text{Cl}_2\text{SiOSiCl}_3(\text{OSiCl}_3(\text{OC}_2\text{H}_5)) + \text{AlCl}_3 \text{ etc.}
\end{align*}
\]

The higher haloesters react less actively with aluminum chloride. Triisoamylchlorosilane at the boiling point, in the presence of aluminum chloride, is decomposed with the formation mainly of isoamylene and isoamyl alcohol (Bibl.12).

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CHAPTER V

SUBSTITUTED ESTERS OF ORTHOSILICIC ACID

The alkyl-(aryl)-substituted esters of orthosilicic acid are one of the most important classes of organosilicon compounds, since they are intermediates in the synthesis of a number of technically valuable polyorganosiloxanes. The first representatives of this class of compounds were prepared as long ago as the 1870's, but the wide utilization of the substituted esters took place only during the last decade, in connection with the result of work by Soviet investigators, which led to the synthesis of high-polymer products which are of great technical value (Bibl.1).

The substituted esters are products of the replacement of one, two, or three alkoxy groups in the molecule of an ester of orthosilicic acid by organic radicals. The following are distinguished:

1. Mono-substituted esters, alkyltrialkoxy-siloxanes $RSi(OR')_3$.
2. Di-substituted esters, dialkyldialkoxy-silanes $R_2Si(OR')_2$.
3. Tri-substituted esters, trialkylalkoxy-silanes $R_3SiOR'$.

In the overwhelming majority of chemical reactions, and especially on hydrolysis, the organic radical connected with the silicon atom is preserved. The hydrolyzates of compounds of the first type therefore belong to the trifunctional monomers, compounds of the second type to the difunctional monomers, and those of the third type to the monofunctional monomers.
METHODS OF PREPARATION

There are three principal methods of preparing substituted esters.

1. Replacement of the alkoxy or aryloxy groups in full esters or of the halogen in halo-esters of orthosilicic acid by organic radicals, by the action of organozinc compounds and sodium.

2. Replacement of the alkoxy groups in full esters or of the halogen in halo-esters of orthosilicic acid by organic radicals, by the action of organomagnesium or organolithium compounds.

3. Esterification of alkyl-(aryl)-chlorosilanes by alcohols or ethylene oxide.

Replacement of Alkoxy Groups by the Action of Organozinc Compounds and Sodium

The substituted esters of orthosilicic acid were first prepared as a result of the reaction of esters or halo-esters or orthosilicic acid with organozinc compounds and metallic sodium.

After Butlerov (Bibl.2) had first prepared organozinc compounds in the 1860's and had performed a large number of synthesis of organic preparations by their aid, Ladenburg (Bibl.3) successfully used diethylzinc and dimethylzinc to prepare substituted esters of orthosilicic acid. The reaction proceeds readily in a sealed tube in the presence of metallic sodium, according to the formula:

\[ 2\text{Si(OC}_3\text{H}_2\text{)}_4 + (\text{C}_2\text{H}_5)_2\text{Zn} + 2\text{Na} \rightarrow 2\text{C}_2\text{H}_5\text{Si(OC}_3\text{H}_2\text{)}_3 + \text{Zn} + 2\text{C}_2\text{H}_5\text{ONa} \]

A similar reaction takes place with the halo-ester of orthosilicic acid:

\[ 2\text{CISi(OC}_3\text{H}_2\text{)}_4 + (\text{C}_2\text{H}_5)_2\text{Zn} + 2\text{Na} \rightarrow 2\text{C}_2\text{H}_5\text{Si(OC}_3\text{H}_2\text{)}_3 + \text{Zn} + 2\text{C}_2\text{H}_5\text{ONa} \]

The replacement of the second alkoxy group is difficult, and takes place on repeated treatment with alkylating agents:

\[ 2\text{C}_2\text{H}_5\text{Si(OC}_3\text{H}_2\text{)}_3 + (\text{C}_2\text{H}_5)_2\text{Zn} + 2\text{Na} \rightarrow 2\text{C}_2\text{H}_5\text{Si(OC}_3\text{H}_2\text{)}_2 + \text{Zn} + 2\text{C}_2\text{H}_5\text{ONa} \]

The product of substitution of three alkoxy groups, which is formed in insig-
significant amounts, has also been isolated:

\[ 2(C_2H_5)_2Si(OC_2H_5)_2 + (C_2H_5)_2Zn + 2Na \rightarrow 2(C_2H_5)_2Si(OC_2H_5)_2 + Zn + 2C_2H_5ONa \]

Tetramethoxysilane (Bibl.4) reacts similarly.

The action of dimethylzinc on tetraethoxysilane was used by Ladenburg to prepare methyltriethoxysilane (Bibl.4).

The synthesis of substituted esters by the reaction of halo-esters or esters of orthosilicic acid with an alkyl halide and metallic sodium is of a certain interest:

\[ (C_4H_9O)_2SiCl_2 + 4Na + 2C_2H_5Br \rightarrow (C_4H_9O)_2Si(C_2H_5)_2 + 2NaCl + 2C_2H_5Br \]

With halo-esters, the reaction proceeds at room temperature, but with esters of orthosilicic acid the reaction is conducted at temperatures above the melting point of sodium:

\[ Si(OC_2H_5)_4 + 2Na + RX \rightarrow R(OC_2H_5)_3 + NaX + C_2H_5ONa \]

**Preparation of Isoaryltrimethoxysilane (Bibl.5).** 1. To a mixture of 1.6 g of sodium, 150 g of tetramethoxysilane and 300 g of toluene, 151 g of isoaryl bromide is added under energetic stirring; the mixture is then held at the boiling point of the solvent for 30 minutes. It is then cooled, filtered, and rectified. The isoaryltrimethoxysilane is collected at 167 - 168°C. Its yield is 39% of theoretical. Isoaryltrimethoxysilanes boils at 108 - 110°C (20 mm); its yield is 25% of theoretical.

Phenytrimethoxysilane, ethyl- and hexylmethoxysilanes are prepared similarly.

2. By a different method (Bibl.6), isoaryltrimethoxysilane is prepared in the following way. A mixture of 21.5 g of SiCl₄ and 57 g of tetramethoxysilane is heated until the boiling point becomes constant at 87°C. To the mixture 152 g of tetraethoxysilane is added, then 23 g of sodium, and the mixture is again heated somewhat above the melting point of sodium for 2 to 4 hours. Then 75.5 g of isoaryl bromide is added to the mixture, after which it is again heated 5 hours; the blue residue is filtered off, and the filtrate is distilled, giving isoaryltrimethoxysilane.
silane, in yield of 43 g.

Under the same conditions a mixture of 15 g of trimethoxysilane, 304 g of tetramethoxysilane, 6 g of metallic sodium, and 51 g of isoamyl bromide is reacted, forming 93.5 g of isoamyltrimethoxysilane and 14 g of diisoamylidimethoxysilane. The reaction is accelerated in the presence of 2 - 10% of ethyl-acetate or of isoamylalcohol. Toluene or xylene are used as solvents.

Synthesis of Phenyltricyclohexyloxysilane. A mixture of 66 g of tricyclohexylchlorosilane and 19.5 g of chlorobenzene is added with stirring to a mixture of 8 g of sodium and 80 g of ethyl ether. A vigorous reaction begins at room temperature in 15 to 30 minutes. After the completion of the exothermic stage of the reaction, the mixture is heated to boiling point for 5 hours, after which the reaction product is filtered and distilled under reduced pressure; boiling point 252 - 253°C (13 mm). The yield is 80% theoretical.

Replacement of Alkoxy Groups by the Action of Organomagnesium and Organolithium Compounds

The difficulty of working with the explosive organozinc compounds forced a search for other methods of preparing substituted esters. The following step in this direction was taken by Khutinskiy and Serezhennkov (Bibl.7), who in 1908 first used organomagnesium compounds in ether for the synthesis of substituted esters.

\[ \text{Si(OCH}_3\text{)}\text{3} + RX \rightarrow Mg \rightarrow \text{RSi(OCH}_3\text{)}\text{2} + \text{C}_6\text{H}_5\text{OMgX} \]

By this method, alkyl-substituted esters and a number of aryl-substituted esters were prepared: phenyltrioethoxysilane, xylyltriethoxysilane, and \( \alpha \) - and \( \beta \) - naphthyltriethoxysilanes. These investigators did not succeed in obtaining di- or tri-substituted esters, and therefore they reached the incorrect conclusion that only mono-substituted esters, \( \text{RSi(OR)}\text{3} \), could be obtained by the aid of organomagnesium compounds.

In 1938 I found (Bibl.1) that the reaction of formation of the organomagnesium
compound could be conducted without use of ether; as a catalyst I used the ethyl ester of orthosilicic acid instead. This facilitated the conduct of the synthesis on a large scale. I was able to prove (Bibl.8) that by selecting proper conditions the process proceeds with high yield; and not only one but two or three alkoxy groups could be substituted.

The reaction product is a mixture of mono-, di-, and tri-substituted esters of orthosilicic acid. The ratio between them depends primarily on the proportions between the starting reagents.

The process may be conducted either in one stage or in two. In the latter case, by the action on magnesium turnings of a mixture of an alkyl halide, a diluent (benzene, toluene, or xylene) and catalytic quantities of tetraethoxysilane, the organomagnesium compound is prepared. The organomagnesium compounds so formed is is used for the reaction with the ester of orthosilicic acid.

The single-stage method of synthesis is more convenient, primarily because it makes it possible easily to direct the reaction towards the formation mainly of the product of the degree of substitution that is required.

Preparation of Ethyltriethoxysilane (Bibl.9). Synthesis in one stage. Into a carefully dried 3-necked flask, provided with a thermometer, a seal and stirrer, a reflux condenser, and a dropping funnel, 12 g of magnesium turnings are placed. A mixture consisting of 64 g of ethyl bromide and 104 g of tetraethoxysilane is then gradually added to the flask from the dropping funnel. The addition takes 3 to 4 hours, with continuous stirring of the reaction mass. Usually, when the first drops of the mixture are added, an exothermic reaction begins, and in order to maintain the necessary temperature (48 - 50°C) of the reaction, the reaction must be conducted under cooling. At the end of the addition of the mixture, the flask is slightly warmed on a water bath. After adding all the mixture, the reaction mass is heated 3 to 4 hours. The liquid is then aspirated into a flask for distillation and is fractionated. The diethylidioethoxysiloxane is collected at 155 - 158°C, and the
ethyltriethoxysilane at 158 - 161°C. The yield of ethyltriethoxysilane is 61% of theoretical.

Synthesis in two stages. In a flask provided with a stirrer, reflux condensor, thermometer and dropping funnel, 12 g of magnesium turnings, 1.5 ml of tetraethoxy-
silane (as a catalyst) are placed, and 34 g of ethylbromide are added dropwise. The reaction is exothermic. Under cooling, a mixture of 30 g of ethyl bromide and 50 g of xylene, toluene, or benzene is added to the contents of the flask. To complete the reaction, the contents of the flask are heated to 40°C for 1 to 1½ hours. The reaction mass is then cooled, and 104 g of tetraethoxysilane is gradually added to it. To complete the reaction, the mixture is then heated 3 hours. The liquid is distilled off and is then rectified. The yield of ethyltriethoxysilane is 58 g, that is, 60.4% of theoretical.

If the object of the synthesis is to prepare diethylidioethoxysilane or dimethyl-
diethoxysilane, the number of moles of the alkylating agents (magnesium and ethyl bro-
mide) per mol of tetraethoxysilane must be correspondingly increased, and the heating after introduction of the mixture must be intensified. In addition, larger amounts of solvent must be used, since the relative quantity of the residue, ethoxymagnesium bromide, will be greater.

It has been found that the substitution of three alkoxy groups proceeds with considerably greater difficulty. Prolonged heating is usually necessary to complete the reaction.

Preparation of trimethylethoxysilane (Bibl.10). Into a solution of 28 mols of methylmagnesium bromide in 12 liters of ethyl ether at a temperature not above 10°C, 8.7 mols of tetraethoxysilane are poured over a period of 30 minutes. The mixture is then warmed for an hour at the boiling point, and the trimethylethoxysilane is then separated by extraction, followed by rectification. The reaction mixture may be subjected to hydrolysis. In this case the ethyl ether is first distilled off; next 70 ml of concentrated sulfuric acid is added to the residue, the mixture is
poured onto ice, and the organic layer is separated, dried, and fractionated, yielding 381 g of hexamethyldisiloxane, which is 54% of theoretical.

Trimethylethoxysilane may be prepared in 78% yield by passing gaseous methyl chloride through a solution of dimethyldiethoxysilane in ethyl ether, mixed with magnesium shavings (Bibl.11).

We have pointed out, above, the relative simplicity and convenience of conducting the synthesis of triethylethoxysilane in a single stage, without using ethyl ether.

Preparation of Triethylethoxysilane (Bibl.12). In a 12-liter flask, a solution of 22 mols of ethylmagnesium bromide in 10 liters of ethyl ether is placed. Into the flask, over the period of 1 hour, 1450 g (7 mols) of tetraethoxysilane is introduced. The mixture is left there for 1 hour with stirring, after which the ether is distilled off and the residue (to complete the alkylation reaction) is heated on a water bath for 12 hours. The triethylethoxysilane can then be separated by extraction and rectification, or it may be hydrolyzed instead.

For hydrolysis, the reaction is poured onto a mixture of ice and sulfuric acid, the product is extracted with ether, and the ether extract is poured under cooling into a flask containing 1.5 liter of sulfuric acid; the organic acid is dried, and the hexaethyldisiloxane is separated by rectification. The yield is 753 g, or 66% of theoretical.

To prepare chemically pure ethylethoxysilanes, the reaction products are separated on a rectification column (with not less than 25 theoretical plates) good results are obtained by rectification on a column 1 m high and 12 mm in diameter, which is packed with single-turn helices 1.2 mm in diameter (of 0.2 mm nichrome wire). The column should have a reflux ratio of 50 to 100. The triethylethoxysilane is collected at 152 - 153°C, the diethylidiethoxysilane at 155 - 156°C, and the ethyltriethoxy- silane at 158 - 159°C. The silicon content and number of ethoxy groups after Zeisel are determined in the products.
By a similar method (without using ethyl ether), butyl- and methyl-substituted esters may be prepared. The process is conducted (Bibl.13) either under atmospheric pressure or in a bomb under a pressure of about 6 atm. The conduct of the process under pressure gives no serious advantages; thus, for example, in the synthesis of butyl-substituted esters, about the same yield is obtained, whether the reaction is conducted under pressure, or without pressure.

Dimethyl-diethoxysilane and methyl-triethoxysilane are obtained in the ratio of 2:1 from tetraethoxysilane, magnesium, and methyl chloride.

A.V. Topchiyev and his associates have described the synthesis of alkoxy derivatives of substituted silanes (Bibl.14). Under the action of phenylmagnesium bromide on tetraethoxysilane, phenyl-triethoxysilane was obtained (Bibl.15). From hexachloromethylene-disilane, under the action of alcohols, hexaalkoxy-methylene-trisilanes have been obtained (Bibl.14).

Hexachloro-ethylene-disilane forms hexaalkoxy-ethylene-disilanes with alcohols:

\[
\text{CH}_2\text{Si(OC}_2\text{H}_5\text{)}_2 + 6\text{ROH} \rightarrow \text{CH}_2\text{Si(OC}_2\text{H}_5\text{)}_2\text{Si(OC}_2\text{H}_5\text{)}_3 + 6\text{H}_2\text{O}
\]

Phenylacetylenetriethoxysilane has been prepared by the reaction (Bibl.16)

\[
\text{C}_6\text{H}_5\text{C}≡\text{CMgBr} + \text{Si(OC}_2\text{H}_5\text{)}_4 \rightarrow \text{C}_6\text{H}_5\text{C}≡\text{CSi(OC}_2\text{H}_5\text{)}_3 + \text{MgBr}
\]

Andrianov and Kamenskaya have synthesised unsaturated substituted esters (Bibl.17).

Preparation of Allyltriethoxysilane. To 24 g of magnesium and 5 g of tetraethoxysilane, a mixture of 121 g of allyl bromide and 208 g of tetraethoxysilane is added dropwise. The reaction mixture is then heated 3 to 4 hours at 100 - 110°C. The liquid is distilled off and rectified, yielding 112.5 g (55.1%) of allyltriethoxysilane. The synthesis of allyltriethoxysilane from tetraethoxysilane, allyl chloride and magnesium is conducted similarly. Yield 50%.

Vol'nov and Reutt have studied the process of preparation of phenylacetylene-
substitute esters:

\[ \text{c}_3\text{H}_5\text{C} \equiv \text{CMgBr} + \text{Si}(\text{OC}_3\text{H}_8)_4 \rightarrow (\text{C}_3\text{H}_5\text{C} \equiv \text{C})_x\text{Si}(\text{OC}_3\text{H}_8)_{4-x} : \text{xH}_4\text{OMgBr} \]

**Preparation of Phenylacetylene-substituted Esters.** Ethylmagnesium bromide is prepared by the action of 154 g of ethylbromide on 36 g of magnesium in the presence of 5 g of tetraethoxysilane. A solution of 152 g of phenylacetylene is then introduced into the reaction flask, and the same amount of xylene. The mixture is heated 3 hours. The reaction mixture is cooled, 325 g of tetraethoxysilane is added to it, and it is then heated for 3 hours. The liquid is then decanted and rectified under reduced pressure. The yield of phenylacetylene triethoxysilane, boiling point 141 - 142°C (6 mm) is 78% of theoretical. A certain quantity of diphenylacetylenedithoxysilane is also formed.

Vol'nov and Reutt noted that phenylacetylene is capable of reacting directly with tetraethoxysilane:

\[ \text{Si}(\text{OC}_3\text{H}_8)_4 + \text{C}_3\text{H}_5\text{C} \equiv \text{CH} \rightarrow \text{C}_3\text{H}_5\text{C} \equiv \text{CSi}(\text{OC}_3\text{H}_8)_3 + \text{C}_4\text{H}_8\text{OH} \]

This reaction is not typical and takes place only owing to the exceptional mobility of the hydrogen atom located around the triple bond in the phenylacetylene. The end product of the reaction is a resin which is formed by the polymerization of the phenylacetylenetriethoxysilane.

The replacement of alkoxy groups by two or three different organic radicals may be accomplished, either by direct alkylation, with separation of the individual intermediate alkylalkoxysilanes, or by successive treatment of tetraethoxysilane with two different organomagnesium compounds. In some cases it is convenient to conduct the reaction even by acting on tetraethoxysilane with magnesium and a mixture of alkyl halides in a solvent.

**Preparation of Methyldiisopropylethoxysilanes (Bibl.18).** Into a solution of 1.3 mols of propylmagnesium chloride in 500 ml of ethyl ether, 104 g of tetraethoxy-
silane is poured. The mixture is stirred 4.5 minutes at room temperature, and then for 8 hours at the boiling point; it is then cooled, 0.6 mol of methylmagnesium chloride dissolved in 250 of ethyl ether is added, and the mixture is then heated again 4 hours at the boiling point. The methyldiisopropylethoxysilane is separated by extraction followed by rectification.

For practical purposes, the possibility of conducting the synthesis, using partially hydrolyzed tetraethoxysilane, has a certain amount of interest, since it is relatively cheap. The partially hydrolyzed tetraethoxysilane is prepared by esterification of SiCl₄ by 95% ethyl alcohol, without subsequent distillation of the reaction products (Bibl.19).

To ethylmagnesium bromide, prepared by pouring a mixture of 1308 g of ethyl bromide and 4 liters of ether onto 288 g of magnesium, 560 g of partially hydrolyzed tetraethoxysilane is added over a period of 4 hours, under cooling. The reaction product is then hydrolyzed by pouring it onto ice; the solvent is distilled off, and the liquid polysiloxanes obtained after completion of the hydrolytic process is distilled under reduced pressure.

The synthesis of substituted esters with complex organic groups by the action of organomagnesium compounds is sometimes not possible; in this case, organolithium compounds must be used instead.

On reaction of tetraethoxysilane with 3.5 equivalents of isopropyllithium in a solution of petroleum ether, the reaction is completed on heating the mixture at boiling point for 24 hours.

\[
\text{Si(OC}_2\text{H}_4)_4 + 3\text{C}_3\text{H}_7\text{Li} \rightarrow 3\text{C}_3\text{H}_7\text{OLi} + (\text{C}_3\text{H}_7)_3\text{SiOC}_2\text{H}_4
\]

The yield of triisopropylethoxysilane is 78% of theoretical (Bibl.20).

The following compounds have been prepared in high yield by this method (Bibl.21):

(C₄H₉)₂Si(OC₂H₄)₂, CH₃(C₄H₉)Si(OC₂H₄)₂, (C₄H₉)₂NC₆H₄Si(OC₂H₄)₂, n-CH₃C₄H₉Si(OC₂H₄)₂, n-CH₂C₄H₉Si(OC₂H₄)₂.
The lower aliphatic lithium alkyl react readily with tetraethoxysilane to form high yields of either substituted esters or tetraalkylsilane (Bibl.22). When tetraethoxysilane reacts with branched lithium alkyls, the steric factor exerts considerable influence, and it is usually not possible to obtain tetra-substituted silanes by using such compounds. For example, when isopropyllithium is used in the reaction given above (Bibl.20), tetraisopropylsilane is not formed.

Under the action of lithium alkyls on substituted esters, substituted esters containing unlike radicals attached to a single silicon atom may be prepared.

Preparation of Substituted Esters from Organohalosilanes

The reaction of organochlorosilanes with alcohol is the usual process for esterification of an acid chloride:

\[ R_xSiCl_{4-x} + (4-x)R'OHH \rightarrow R_xSi((OR')_{4-x} + (4-x)HCl \]

This reaction is not fundamentally different from the esterification of SiCl\(_4\); the process is distinguished only by its low intensity, while, for instance, the activity of organochlorosilanes is lower, the higher the molecular weight of the organo radicals and the greater the number of such radicals in the molecule. The esterification is accompanied by side processes; formation of water, owing to the reaction of HCl with the alcohol, and formation of polymeric products of hydrolysis.

\[ RCH + HCl \rightarrow \rightarrow RCl + H_2O \]

\[ 2R_xSiCl_2 + H_2O \rightarrow \rightarrow ClR_xSi-O-SiR_xCl + 2HCl \]

The side reactions are of less importance when butyl and higher alcohols are used, and for this reason esterification with butyl or isobutyl alcohols is in practice the most convenient.

Preparation of Methylbutoxyasilanes (Bibl.23). To a mixture consisting of
3.82 kg of dimethylchlorosilane and 0.33 kg of methyltrichlorosilane, 5.8 kg of butanol is added over a period of 8 hours. Then, to complete the process, the mixture is heated to 90°C until the evolution of HCl ceases. The reaction mixture is then rectified, giving dimethyldibutoxysilane, with a boiling point of 75% (10 mm), in yield of 67% of theoretical, and methyltributoxysilane, boiling point 115°C (10 mm).

In this way a mixture of methylchlorosilanes, which is very difficult to separate, may be converted into substituted esters, after which the individual products can be separated.

When dimethylchlorosilane reacts with an equimolecular quantity of butanol, dimethylbutoxysilane can be obtained in 61% yield as the product of partial esterification.

On the esterification of trimethylchlorosilane by butyl, ethyl, or methyl alcohols, the separation of the reaction products is difficult owing to the fact that they form azeotropic mixtures with the corresponding alcohol. Thus (Bibl.24), on esterification of 5.4 g of trimethylchlorosilane in 100 ml of toluene by a solution of 20 ml of absolute methanol in 50 ml of pyridine (to neutralize the HCl evolved), a mixture is formed, giving on rectification 14.5 g of an azeotrope of trimethylmethoxysilane and methanol (14 - 16%) (the boiling point of azeotropic mixture is 49 - 50°C; the index of refraction nD20 = 1.3637), and 7.4 g of trimethylmethoxysilane, with a boiling point of 56.5 - 56.7°C (767 mm).

When ethanol is used as the solvent, the yield of trimethylmethoxysilane is increased to 14%. Trimethylethoxysilane similarly forms an azeotropic mixture with ethanol (boiling point of the azeotropic mixture 66°C; refractive index nD20 = 1.3729), while trimethylbutoxysilane forms an azeotropic mixture with butanol (40 - 44%) (boiling point of azeotropic mixture 111 - 115°C; nD20 = 1.3963).

A number of other substituted ethoxysilanes - phenyl (Bibl.25), propyl, isomyl, benz-1, naphthyl (Bibl.26) - have been prepared by esterification of the correspond-
in, substituted chlorosilanes by ethanol.

The water-soluble esters are prepared by esterification of alkyl-(aryl)-chlorosilanes by simple esters of glycol: α-ethoxyethanol (Bibl.27). Esterification of the alkylchlorosilanes is conducted by reacting them with an excess of the alcohol at the boiling point of the alkylchlorosilane, followed by boiling the mixture to remove the HCL. The di- and mono-substituted methoxy derivatives, \( R_2Si(OCH_2CH_2)_2 \) and \( R_3Si(OCH_3)_3 \), are usually completely soluble in water, while the corresponding ethoxy derivatives, \( R_xSi(OCH_2H_4OCH_2H_5)_{4-x} \), are somewhat less soluble. The aqueous solution remains transparent for half an hour, and is only slightly hydrolyzed in 24 hours. The presence of acid or alkali leads to rapid hydrolysis.

On the reaction of esterification of organochlorosilanes containing a bromine atom in the organic radical, this bromine does not enter into the reaction (Bibl.28).

\[
BrC_4H_4SiCl_3 + 3ROH \rightarrow BrC_4H_4Si(OR)_3
\]

where \( R = CH_3, C_2H_5, C_4H_9 \). The yield is about 50%.

To eliminate the side reactions due to the evolution of HCL, esterification is conducted either in the presence of neutralizing agents, or in such a way that HCL is not formed during the reaction, for example, by the action of sodium alcoholate on alkylchlorosilanes (Bibl.29):

\[
R_xSiCl_{4-x} + (4-x)CH_3ONa \rightarrow R_xSi(OCH_3)_{4-x} + (4-x)NaCl
\]

Another method of esterification, without formation of HCL, is based on the reaction of the organochlorosilane with ethylene oxide:

\[
R_xSiCl_{4-x} + (4-x)CH_2CH_2O \rightarrow R_xSi(OCH_2CH_2CH_2)_{4-x}
\]

This process apparently takes place in two stages.

In the first stage, which is the rate-determining stage, the HCL that is always present in certain quantities in alkylchlorosilanes, adds to the ethylene oxide.
The chlorohydrin formed in the second stage esterifies the alkylchlorosilane, which step is accompanied by the regeneration of HCl. Such a mechanism is in agreement with the fact that the velocity of the process is considerably increased in the presence of HCl.

At the present time the possibility of conducting a reaction in the absence of traces of HCl has not yet been established.

The esterification of organochlorosilanes by ethylene oxide is effected either by passing bubbles of the gas through the chlorosilane at an elevated temperature in a flask with a reflux condenser cooled by ice water, or at elevated pressure by pumping ethylene oxide into an autoclave at a temperature of about 60°C. The reaction products are rectified under reduced pressure. The yield, as a rule, is 80 - 95% of theoretical (Bibl.30).

The vinylalkoxyxilanes and the vinylaryloxysilanes have been prepared by the action of alcohols, phenol, methoxyethylene or ethylene chlorohydrin on vinyltrichlorosilane (Bibl.31). It is also noted that acetic anhydride reacts with β-chloroethylalkoxysilane to form the compound \( \text{CH}_3\text{COOSi(OR)}_2\text{CH}_2\text{CH}_2\text{Cl} \), while propionic anhydride forms the compound \( \text{C}_2\text{H}_5\text{COOSi(OR)}_2\text{CH}_2\text{CH}_2\text{Cl} \). The diacetate can also be prepared.

On the partial hydrolysis of α-chloroethytltrialkyloxysilanes, di-α-chloroethyl-tetraalkoxydisiloxanes are formed (Bibl.32).

As has already been stated, the reaction of an alcohol with \( \text{SiF}_4 \) proceeds considerably more slowly than with \( \text{SiCl}_4 \). The esterification of alkylfluorosilanes likewise proceeds considerably more slowly than that of alkylchlorosilanes.

When 0.268 mol of ethanol and 0.131 mol of phenyldichlorofluorosilane react for 20 minutes at 23 - 40°C, diethoxyphenylfluorosilane is formed, which indicates that the activity of the Si-F bond on esterification is lower than that of the Si-Cl bond. The esterification of alkylfluorosilanes does not as a rule proceed to completion.
It is possible to accomplish this completion by neutralizing the hydrofluoric acid formed.

**Preparation of Tripropylethoxysilane (Bibl.18).** In 70 g of absolute ethanol 3 g of metallic sodium are placed, and a solution of 21 g of tripropylfluorosilane in 50 ml of petroleum ether is then added. The sodium fluoride so formed is washed away with water; and the product is dried and distilled. The yield of unpurified tripropylethoxysilane is almost quantitative.

The alkyl-(aryl)-bromosilanes react like the alkyl-(aryl)-chlorosilanes. For instance, dimethylbromosilane reacts very energetically with ethylene oxide under a pressure of 2.2 atm. The process is completed under a pressure of 5.5 atm, and the autoclave is periodically cooled in a water bath. The yield of dimethyl-di-(β, β'-bromoethoxy)-silane is 48.8 g, or (89%). Methyl-β, β'-tri(bromethoxy)-silane is prepared similarly.

It is convenient to use the reaction of alcoholysis to prepare substituted esters with alkoxy groups of higher molecular weight than the ethoxy groups, and also with unsaturated alkoxy groups. The process conditions and the catalyst are the same as in the reaction, already described, of alcoholysis of esters of orthosilicic acid.

On treatment of amyltriethoxysilane with allyl alcohol, amyltriallyloxysilane is formed:

\[ C_3H_7Si(OCH_2CH_3)_3 + 3CH_2=CHCH(OH) \rightarrow C_4H_9Si(OCH_2-CH\_CH_2) + 3C_2H_5OH \]

Propyl, butyl, isobutyl, and isoamyl alcohols, on prolonged heating with ethyl- or phenyltriethoxysilane, form the respective ethyl- or phenyl-substituted esters (Bibl.33).

**Preparation of Amylallyloxysilanes.** A mixture of 46.9 g of amyltriethoxysilane, 69.7 g of allyl alcohol, and 3 drops of SiCl₄, is heated in the retort of a rectifying column for 4 hours, at the same time distilling off the ethanol. Rectification of the reaction product yields 46.9 g (84%) of amyltriallyloxysilane, having the
melting point of 153.5°C. When allyltrithoxysilane reacts with amyl alcohol, allyl-
trimyloxysilane is formed in yield of 61% of theoretical. Dimyldiallyloxysilane is
prepared similarly, in yield 81% of theoretical (Bibl.34).

Physical Properties

The substituted ether esters of orthosilicic acid are colorless liquids which
can be distilled under atmospheric pressure without decomposition. The high-boiling
compounds are distilled under reduced pressure. They are readily soluble in alcohol,
aromatic hydrocarbons, chlorinated hydrocarbons, ketones, and ethers. They burn,
giving off a white smoke (suspended particles of SiO₂). They are not miscible with
water. Some substituted esters of orthosilicic acid form azeotropic mixtures with
alcohols and aromatic hydrocarbons.

Table 40 gives the physical properties of monoalkyl- and monoaryl-substituted
esters, halo-esters and anhydrides of orthosilicic acid.

As will be seen from Table 40, they are difficultly crystallizable liquids. Even
the high-boiling products are still difficult to crystallize.

Table 41 gives the physical properties of di-substituted esters, halo-esters and
anhydrides of orthosilicic acid. Table 43 gives the properties of tri-substituted
esters and anhydrides of orthosilicic acid.

CHEMICAL PROPERTIES

The chemical properties of the substituted ethers are determined primarily by
the presence in their molecules of the hydrolytically unstable Si-OC bonds. The or-
ganic radical attached to the silicon atom is preserved in most chemical reactions,
and therefore, with respect to the direction of the reaction, the substituted esters
behave like the esters of orthosilicic acid Si(OR)₄. The presence of an organic rad-
ical attached to the silicon atom, however, gives the molecule of a substituted es-
ter a higher stability against the action of chemical reagents. The similarity and
Table 40

Physical Properties of Mono-Substituted Esters, Halo-Esters and Anhydrides of Orthosilicic Acid

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>B.P. °C</th>
<th>Spec. Grav. d₂₀</th>
<th>Refr. Index n₂₀</th>
<th>Bibl.</th>
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<td>Methyltrimethoxysilane</td>
<td>CH₃Si(OCH₃)₃</td>
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<td>CH₃Si(OCH₂CH₃)₂</td>
<td>151-145</td>
<td>0.9363</td>
<td>1.3861</td>
<td>3.67</td>
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<tr>
<td>Methyltriisobutoxysilane</td>
<td>CH₃Si(OCH₂CH₂CH₃)₃</td>
<td>115</td>
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<td>Methyltri-β-chloroethoxysilane</td>
<td>CH₃Si(OCH₂CH₂Cl)₃</td>
<td>137</td>
<td>1.257</td>
<td>1.4562</td>
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<tr>
<td>Methyltri-β-bromoethoxysilane</td>
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<td>1.27</td>
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<td>Methyltriacetoxyisilane</td>
<td>CH₃Si(OOCH₃)₂</td>
<td>89-94</td>
<td>1.407</td>
<td></td>
<td>28.30</td>
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<tr>
<td>Methyltri-β-methoxyethoxysilane</td>
<td>CH₃Si(OCH₂CH₂OCH₃)₃</td>
<td>145</td>
<td>1.0454</td>
<td>1.4200</td>
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<td>Trichloromethyltriethoxysilane</td>
<td>CCl₃Si(OCH₂CH₃)₂</td>
<td>81</td>
<td>1.8660</td>
<td>1.4390</td>
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<td>Vinyltri-β-(chloromethoxy) silane</td>
<td>CH₃=CHSi(OCH₂CH₂Cl)₃</td>
<td>152-153</td>
<td>1.2462</td>
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<td>81</td>
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<td>Vinyltri-(β-methoxyethoxy) silane</td>
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<td>Vinyltriallyoxyisilane</td>
<td>CH₃=CHSi(OCH₂CH₂CH₂)₂</td>
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<td>0.9435</td>
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<td>CH₃=CHSi(OCH₂CH₂CH₂CH₂)₃</td>
<td>136.8</td>
<td>0.8738</td>
<td>1.4242</td>
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<td>Vinyltrihexyloxyisilane</td>
<td>CH₃=CHSi(OCH₂CH₂CH₂CH₂CH₂)₂</td>
<td>177-179</td>
<td>0.87191</td>
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<tr>
<td>Vinyltrihexylenoxyisilane</td>
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<td>0.89061</td>
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<td>Vinyltrioctyloxyisilane</td>
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<td>223-226</td>
<td>0.8639</td>
<td>1.4400</td>
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<td>Vinyltriphenoxysilane</td>
<td>CH₃=CHSi(OCH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂)₂</td>
<td>210.2</td>
<td>1.10604</td>
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<td>α-Bromovinyltriethoxysilane</td>
<td>CH₂=BrSi(OCH₂CH₂)₂</td>
<td>77-79.5</td>
<td>1.4900</td>
<td>1.4252</td>
<td>81</td>
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<td>α-Bromovinyltrimethyl oxyisilane</td>
<td>CH₂=BrSi(OCH₂CH₂)₂</td>
<td>74-75</td>
<td>1.22191</td>
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<td>α-Chlorovinyltriethoxysilane</td>
<td>CH₂=ClSi(OCH₂CH₂)₂</td>
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<td>1.02314</td>
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<td>β,β-Dichlorovinyltrimethoxysilane</td>
<td>CH₂=ClSi(OCH₂CH₂)₂</td>
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<td>1.4421</td>
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<td>β,β-Dichlorovinyltriethoxysilane</td>
<td>CH₂=ClSi(OCH₂CH₂)₂</td>
<td>164</td>
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<th>Refr. Index n²₀³₂</th>
<th>Bibl.</th>
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<td>Ethyltrimethoxysilane</td>
<td>C₄H₅Si(OCH₃)₃</td>
<td>126</td>
<td>0.9747</td>
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<td>Ethyltriethoxysilane</td>
<td>C₄H₅Si(OCH₂CH₃)₂</td>
<td>120.6</td>
<td>0.9207</td>
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<td>Ethyltripropoxysilane</td>
<td>C₄H₅Si(OCH₃(CH₃)₂)</td>
<td>202</td>
<td>0.886</td>
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<td>C₄H₅[OCH₂(CH₂CH₂)₂Si]</td>
<td>102</td>
<td>1.1891</td>
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<td>Ethyltrimethoxysilane</td>
<td>C₄H₅Si(OCH₃)₃</td>
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<td>α,β-Dichoroethyltrimethoxysilane</td>
<td>C₅H₅Cl₂Si(OCH₃)₂</td>
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<td>α,β-Dibromomethyltrimethoxysilane</td>
<td>C₅H₅Br₂Si(OCH₃)₂</td>
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<td>1.4430</td>
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<td>C₅H₅Br₂Si(OCH₃)₂</td>
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<td>1.6637</td>
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<td>1.033</td>
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<td>C₅H₅Cl₂Si(OCH₂CH₂CH₃)₂</td>
<td>121.6</td>
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<td>C₅H₅Cl₂Si(OCH₂CH₃)₂</td>
<td>116</td>
<td>0.9828</td>
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<td>C₅H₅Cl₂Si(OCH₂CH₃)₂</td>
<td>137</td>
<td>0.9672</td>
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<td>β-Chloroethyltrimethoxyacetoxy silane</td>
<td>C₅H₅Cl₂Si(OCH₂CH₃)₂</td>
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<td>1.161</td>
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<td>C₅H₅Cl₂Si(OCH₂CH₃)₂</td>
<td>117</td>
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<td>122</td>
<td>1.052</td>
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<td>β-Chloroethyl dimethoxyacetoxysilane</td>
<td>CICH₂(CH₂)₂Si(OCH₃)₂(CH₂)₃OC(OCH₃)₃</td>
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<td>1.000</td>
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<td>β-Chloroethylmethoxydiacetoxysilane</td>
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<td>1.129</td>
<td>1.4241</td>
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<td>CICH₂(CH₂)₂SiOC(OCH₃)₃(CH₂)₃OC(OCH₃)₃</td>
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<td>CICH₂(CH₂)₂SiOC(OCH₃)₃(CH₂)₄OC(OCH₃)₃</td>
<td>100.1</td>
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<td>0.8528</td>
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<td>91.92</td>
<td>1.110</td>
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<td>Butyltriethoxysilane</td>
<td>C₆H₄Si(CH₂)₂OC(OCH₃)₃(CH₂)₃OC(OCH₃)₃</td>
<td>190-195</td>
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<td>Isobutyltriethoxysilane</td>
<td>(CH₃)₂CH(CH₂)SiOC(OCH₃)₃(CH₂)₃OC(OCH₃)₃</td>
<td>167.108</td>
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<td>Isobutyltriisocetoxy silane</td>
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<td>153.5</td>
<td>1.4383</td>
<td>5.8</td>
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<tr>
<td>Amyltriethoxysilane</td>
<td>(CH₃)₂CH(CH₂)⁶SiOC(OCH₃)₃(CH₂)₃OC(OCH₃)₃</td>
<td>108</td>
<td>0.936</td>
<td>1.3982</td>
<td>8</td>
</tr>
<tr>
<td>Isoamyldiethoxysilane</td>
<td>(CH₃)₂CH(CH₂)ⁿSiOC(OCH₃)₃(CH₂)₃OC(OCH₃)₃</td>
<td>108</td>
<td>0.936</td>
<td>1.3982</td>
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<td>Hexyltriethoxysilane</td>
<td>C₆H₅Si(CH₂)₂OC(OCH₃)₃(CH₂)₃OC(OCH₃)₃</td>
<td>258-259</td>
<td>1.0138</td>
<td>15.21</td>
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<td>Phenyltrimethoxysilane</td>
<td>C₆H₅Si(CH₂)₂OC(OCH₃)₃(CH₂)₃OC(OCH₃)₃</td>
<td>192</td>
<td>0.946</td>
<td>1.3925</td>
<td>8</td>
</tr>
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<td>Phenyltripropoxysilane</td>
<td>C₆H₅Si(CH₂)₄OC(OCH₃)₃(CH₂)₃OC(OCH₃)₃</td>
<td>156</td>
<td>0.946</td>
<td>1.3925</td>
<td>8</td>
</tr>
<tr>
<td>Phenyltriisobutoxysilane</td>
<td>C₆H₅Si(CH₂)₄OC(OCH₃)₃(CH₂)₃OC(OCH₃)₃</td>
<td>196</td>
<td>0.946</td>
<td>1.3925</td>
<td>8</td>
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<td>Phenyltriisoamyloxy silane</td>
<td>C₆H₅Si(CH₂)₄OC(OCH₃)₃(CH₂)₃OC(OCH₃)₃</td>
<td>158</td>
<td>1.2080</td>
<td>13.5077</td>
<td>9</td>
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<td>Phenyltri-(β-chloroethoxy)-silane</td>
<td>C₆H₅Si(CH₂)₄OC(OCH₃)₃(CH₂)₃OC(OCH₃)₃</td>
<td>204</td>
<td>1.0818</td>
<td>1.1727</td>
<td>25</td>
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<td>B.P. °C</td>
<td>Spec. Grav. d&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Refr. Index n&lt;sub&gt;D&lt;/sub&gt;</td>
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<td>Phenyltricyclohexyloxy-silane</td>
<td>C&lt;sub&gt;11&lt;/sub&gt;H&lt;sub&gt;13&lt;/sub&gt;Si(OCH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>252-253</td>
<td>-</td>
<td>-</td>
<td>8</td>
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<tr>
<td>Phenyltriphenoxysilane</td>
<td>C&lt;sub&gt;11&lt;/sub&gt;H&lt;sub&gt;15&lt;/sub&gt;Si(OCH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>248-250</td>
<td>-</td>
<td>-</td>
<td>7</td>
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<tr>
<td>Phenyldiethoxyfluorosilane</td>
<td>C&lt;sub&gt;11&lt;/sub&gt;H&lt;sub&gt;13&lt;/sub&gt;Si(OF&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>64-75</td>
<td>-</td>
<td>-</td>
<td>18</td>
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<tr>
<td>p-Bromophenyltrimethoxysilane</td>
<td>BrC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;Si(OCH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>136</td>
<td>1.3493 (13.5 mm)</td>
<td>1.5121 (16.5°)</td>
<td>28</td>
</tr>
<tr>
<td>p-Bromophenyltriethoxysilane</td>
<td>BrC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;Si(OCH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>150</td>
<td>1.2244 (12 mm)</td>
<td>1.4925 (15.4°)</td>
<td>28</td>
</tr>
<tr>
<td>p-Bromophenyltripropoxy-silane</td>
<td>BrC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;Si(OCH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>178</td>
<td>1.1553 (14 mm)</td>
<td>1.4907 (16.6°)</td>
<td>28</td>
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<tr>
<td>p-Bromophenyltrimobutoxy-silane</td>
<td>BrC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;Si(OCH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>191</td>
<td>1.0923 (14 mm)</td>
<td>1.4765 (14.9°)</td>
<td>28</td>
</tr>
<tr>
<td>p-Aminophenyltriethoxy-silane</td>
<td>NH&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;Si(OCH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>148</td>
<td>-</td>
<td>-</td>
<td>21</td>
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<tr>
<td>p-Dimethylaminophenyltriethoxy-silane</td>
<td>(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;NCH&lt;sub&gt;3&lt;/sub&gt;Si(OCH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>180-182</td>
<td>-</td>
<td>-</td>
<td>21</td>
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<tr>
<td>p-Tolyldiethoxysilane</td>
<td>C&lt;sub&gt;9&lt;/sub&gt;H&lt;sub&gt;14&lt;/sub&gt;Si(OCH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>137</td>
<td>-</td>
<td>-</td>
<td>21</td>
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<tr>
<td>Benzyltriethoxysilane</td>
<td>C&lt;sub&gt;9&lt;/sub&gt;H&lt;sub&gt;14&lt;/sub&gt;Si(OCH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>248-250</td>
<td>0.8631 (28 mm)</td>
<td>0.8684 (26°)</td>
<td>26</td>
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<td>Phenylenethynyltriethoxy-silane</td>
<td>C&lt;sub&gt;12&lt;/sub&gt;H&lt;sub&gt;16&lt;/sub&gt;-C≡CSi(OCH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>141-142</td>
<td>0.986 (22°)</td>
<td>1.4986 (71°)</td>
<td>71</td>
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<tr>
<td>2,4-Dimethylphenyltriethoxy-silane</td>
<td>(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;Si(OCH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>270</td>
<td>-</td>
<td>-</td>
<td>7</td>
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<td>1,5-Dimethylphenyltriethoxy-silane</td>
<td>(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;Si(OCH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>150</td>
<td>-</td>
<td>-</td>
<td>21</td>
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<tr>
<td>p-Biphenyltriethoxy-silane</td>
<td>C&lt;sub&gt;12&lt;/sub&gt;H&lt;sub&gt;14&lt;/sub&gt;Si(OCH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>210-215</td>
<td>-</td>
<td>-</td>
<td>21</td>
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<tr>
<td>Cyclohexyltriethoxy-silane</td>
<td>C&lt;sub&gt;12&lt;/sub&gt;H&lt;sub&gt;14&lt;/sub&gt;Si(OCH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>233-234</td>
<td>-</td>
<td>-</td>
<td>8</td>
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<tr>
<td>a-Naphthyltriethoxy-silane</td>
<td>C&lt;sub&gt;14&lt;/sub&gt;H&lt;sub&gt;16&lt;/sub&gt;Si(OCH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>220-230</td>
<td>1.4332 (718 mm)</td>
<td>1.9330 (19.5°)</td>
<td>8</td>
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<td></td>
<td></td>
<td>308-320</td>
<td>(19.5°)</td>
<td>(744 mm)</td>
<td>7</td>
</tr>
<tr>
<td>β-Naphthyltriethoxy-silane</td>
<td>C&lt;sub&gt;14&lt;/sub&gt;H&lt;sub&gt;16&lt;/sub&gt;Si(OCH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>175</td>
<td>-</td>
<td>-</td>
<td>7</td>
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<td>Dodecyltriethoxy-silane</td>
<td>C&lt;sub&gt;16&lt;/sub&gt;H&lt;sub&gt;32&lt;/sub&gt;Si(OCH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>270-273</td>
<td>-</td>
<td>-</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>140-160</td>
<td>-</td>
<td>-</td>
<td>80</td>
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<tr>
<td>Name</td>
<td>Formula</td>
<td>B.P. °C</td>
<td>Spec. Grav.</td>
<td>Refr. Index nD</td>
<td>Bibl.</td>
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<td>Dimethyldioethoxysilane</td>
<td>(CH3)2Si(OC2H5)2</td>
<td>111-114</td>
<td>0.890</td>
<td>1.3839</td>
<td>67.68</td>
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<td>Dimethylz-(β-chloroethoxy)-silane</td>
<td>(CH3)2Si(OC2H4Cl)2</td>
<td>213</td>
<td>1.135</td>
<td>1.4420</td>
<td>30</td>
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<td>Dimethylz-(β-bromoethoxy)-silane</td>
<td>(CH3)2Si(OC2H4Br)2</td>
<td>92</td>
<td>-</td>
<td>30</td>
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<tr>
<td>Dimethyldibutoxysilane</td>
<td>(CH3)2Si(OCH2)2</td>
<td>187</td>
<td>-</td>
<td>1.4058</td>
<td>73</td>
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<td>Dimethylbutoxychlorosilane</td>
<td>(CH3)2Si(OCH2Cl)</td>
<td>100</td>
<td>-</td>
<td>73.34</td>
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<td>Dimethyldiacetoxy silane</td>
<td>(CH3)2Si(OCH3)2</td>
<td>44-45</td>
<td>1.0485</td>
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<td>29</td>
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<td>Dimethylz-(β-methoxyethoxy)-silane</td>
<td>(CH3)2Si(OCH2)2</td>
<td>203-204</td>
<td>0.9663</td>
<td>1.1414</td>
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<td>Dimethylz-(β-ethoxyethoxy)-silane</td>
<td>(CH3)2Si(OC2H4)2</td>
<td>136</td>
<td>0.9369</td>
<td>1.1431</td>
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<td>Dimethylmethoxysilane</td>
<td>(CH3)2Si(OC3H7)2</td>
<td>128.1</td>
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<td>Dimethyldioethoxysilane</td>
<td>(CH3)2Si(OC2H4)2</td>
<td>155-156</td>
<td>0.8752</td>
<td>-</td>
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<td>Dimethylzethoxychlorosilane</td>
<td>(CH3)2Si(OC2H4Cl)2</td>
<td>147.149</td>
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<td>3.71</td>
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<td>Diethyldialyloxysilane</td>
<td>(CH2)2Si(OC2H4)2</td>
<td>74-72</td>
<td>1.0190</td>
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<td>Diethyldiphenoxysilane</td>
<td>(CH3)2Si(OC6H5)2</td>
<td>130-152</td>
<td>-</td>
<td>68</td>
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<td>Dimethylzethoxy silane</td>
<td>(CH2)2Si(OC2H4)2</td>
<td>186</td>
<td>187</td>
<td>1.4130</td>
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<td>Diphenyldioethoxysilane</td>
<td>(C6H5)2Si(OC2H4)2</td>
<td>220</td>
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<td>Dibutyldioethoxysilane</td>
<td>(C6H5)2Si(OC2H4)2</td>
<td>82</td>
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<td>5.8</td>
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<td>Diisopropyldioethoxysilane</td>
<td>(C6H5)2Si(OC2H4)2</td>
<td>108-110</td>
<td>1.4415</td>
<td>8.34</td>
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<td>Diethyldiethoxysilane</td>
<td>(C6H5)2Si(OC2H4)2</td>
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<td>0.9415</td>
<td>8.34</td>
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<td>Diphenylzethoxychlorosilane</td>
<td>(C6H5)2Si(OC2H4)2</td>
<td>302-304</td>
<td>217-218</td>
<td>72</td>
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<td>Diphenyldi-β-chloroethoxy- silane</td>
<td>(C6H5)2Si(OC2H4Cl)2</td>
<td>130-152</td>
<td>-</td>
<td>72</td>
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<tr>
<td>Diphenyldiethoxy silane</td>
<td>(C6H5)2Si(OC2H4)2</td>
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<td>Diphenylmethoxychlorosilane</td>
<td>(C6H5)2Si(OC2H4Cl)2</td>
<td>220</td>
<td>-</td>
<td>5.8</td>
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<td>Di-(phenylethynyl)-diethoxy- silane</td>
<td>(C6H5)2Si(OC2H4)2</td>
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<td>1.2027</td>
<td>1.5105</td>
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<td>Diphenylphenoxysilane</td>
<td>(C6H5)2Si(OC2H4)2</td>
<td>190</td>
<td>-</td>
<td>73.74</td>
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<td>Di-(phenylethynyl)-diethoxy- silane</td>
<td>(C6H5)2Si(OC2H4)2</td>
<td>253</td>
<td>-</td>
<td>73</td>
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<td>Di-(oxyethylphenyl)-diethoxy- silane</td>
<td>(C6H5)2Si(OC2H4)2</td>
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<td>1.329</td>
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<td>Dibenzyldibutoxysilane</td>
<td>(C6H5)2Si(OCH2)2</td>
<td>206-207</td>
<td>1.5234</td>
<td>75</td>
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<td>Dibenzyldiphenoxysilane</td>
<td>(C6H5)2Si(OC6H5)2</td>
<td>230</td>
<td>1.1164</td>
<td>1.5922</td>
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<td>Formula</td>
<td>B.P. °C</td>
<td>Spec. Grav. ρ20</td>
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<td>Methylbenzyl di-(β-methoxy) - silane</td>
<td>(CH₃)₃C₆H₃(CH₃)Si(O(CH₂)₄OC₂H₄)₂ 181-185</td>
<td>1.041</td>
<td>1.4795</td>
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<td>27</td>
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<td></td>
<td>CH₃SiH(O(CH₂)₄OC₂H₄)₂ (15 mm) 96</td>
<td>1.1643</td>
<td>1.4431</td>
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<td>28-30</td>
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<td>CH₃SiH(O(CH₂)₄OC₂H₄)₂ (18 mm) 84-84</td>
<td>-</td>
<td>-</td>
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<td>CH₃SiH(O(CH₂)₄OC₂H₄)₂ (45 mm) 140</td>
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<td>1.3500</td>
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<td>CH₃(C₂H₅)Si(O(CH₂)₄OC₂H₄)₂ 146-152</td>
<td>0.9454</td>
<td>1.4298</td>
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<td>CH₃(C₂H₅)Si(O(CH₂)₄OC₂H₄)₂ (15 mm) 221.5</td>
<td>-</td>
<td>-</td>
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<td>21</td>
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<tr>
<td></td>
<td>CH₃(C₂H₅)Si(O(CH₂)₄OC₂H₄)₂ (105-110) 135 mm</td>
<td>-</td>
<td>-</td>
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<td>21</td>
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<tr>
<td>Methylphenyl di-(β-methoxy) - silane</td>
<td>C₄H₉(C₆H₅)Si(O(CH₂)₄OC₂H₄)₂ 201</td>
<td>1.2488</td>
<td>1.5531</td>
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<td>28</td>
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<td></td>
<td>C₄H₉(C₆H₅)Si(O(CH₂)₄OC₂H₄)₂ (17 mm) 201</td>
<td>-</td>
<td>-</td>
<td></td>
<td>76</td>
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<td></td>
<td>C₄H₉(C₆H₅)Si(O(CH₂)₄OC₂H₄)₂ (20 mm) 103-104</td>
<td>-</td>
<td>-</td>
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<td>76</td>
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<tr>
<td>Phenylbromophenyl diethoxy silane</td>
<td>C₄H₉Br(C₆H₅)Si(O(CH₂)₄OC₂H₄)₂ 103-104</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Phenylcyclohexyl diethoxy xilane</td>
<td>C₄H₉(C₆H₄)Si(O(CH₂)₄OC₂H₄)₂ 103-104</td>
<td>-</td>
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Table 42
Properties of Mixtures of Certain Substituted Esters of Orthosilicic Acid with Alcohols (Bibl. 24, 80)

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<tr>
<th>Substituted Esters</th>
<th>Alcohol</th>
<th>B.P. of Mixture °C</th>
<th>Refr. Index nD</th>
<th>Alcohol Content of Mixture, %</th>
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<tr>
<td>(CH₂)₃SiOCH₃</td>
<td>CH₃OH</td>
<td>50</td>
<td>1.3637</td>
<td>14—16</td>
</tr>
<tr>
<td>(CH₂)₃SiOC₂H₅</td>
<td>C₂H₅OH</td>
<td>66</td>
<td>1.3729</td>
<td>—</td>
</tr>
<tr>
<td>(CH₂)₃SiOCH₂CH(CH₃)₂</td>
<td>(CH₂)₃CHCH₂OH</td>
<td>111</td>
<td>1.3963</td>
<td>40—44</td>
</tr>
</tbody>
</table>

Table 43
Physical Properties of Tri-Substituted Esters and Anhydrides of Orthosilicic Acid

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>B.P. °C</th>
<th>Spec. Grav.  d₄¹⁰</th>
<th>Refr. Index nD ₂⁰</th>
<th>Bibl.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trimethylmethoxysilane</td>
<td>(CH₂)₃SiOC₂H₅</td>
<td>57,2 (747 mm)</td>
<td>—</td>
<td>1.3679</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>56.5—56.7</td>
<td>—</td>
<td>1.3678</td>
<td>24</td>
</tr>
<tr>
<td>Triethylethoxysilane</td>
<td>(CH₂)₃SiOCH₃</td>
<td>75 (745 mm)</td>
<td>0.7573</td>
<td>1.3741</td>
<td>10,24</td>
</tr>
<tr>
<td>Triethylbutoxysilane</td>
<td>(CH₂)₃SiOC₂H₅</td>
<td>123</td>
<td>0.7774</td>
<td>1.3925</td>
<td>24</td>
</tr>
<tr>
<td>Triethyl-β-chloroethoxysilane</td>
<td>(CH₂)₃SiOC₂H₅ Cl</td>
<td>134,3 (761 mm)</td>
<td>0.9443</td>
<td>1.4140</td>
<td>30</td>
</tr>
<tr>
<td>Triethylethoxysilane</td>
<td>(CH₂)₃SiOCH₃</td>
<td>153</td>
<td>0.8414</td>
<td>—</td>
<td>30</td>
</tr>
<tr>
<td>Triethylacetoxysilane</td>
<td>(CH₂)₃SiOCH₃</td>
<td>154</td>
<td>0.8310 (25.5%)</td>
<td>1.4714</td>
<td>24</td>
</tr>
<tr>
<td>Tripropylethoxysilane</td>
<td>(C₃H₇)₂SiOCH₃</td>
<td>198—200 (738 mm)</td>
<td>0.8657</td>
<td>1.4560</td>
<td>33</td>
</tr>
<tr>
<td>Tripropylacetoxysilane</td>
<td>(C₃H₇)₂SiOCH₃</td>
<td>212—216 (738 mm)</td>
<td>0.8657</td>
<td>1.4560</td>
<td>33</td>
</tr>
<tr>
<td>Triisopropylethoxysilane</td>
<td>(C₃H₇)₂SiOCH₃</td>
<td>—</td>
<td>0.8657</td>
<td>1.4560</td>
<td>33</td>
</tr>
<tr>
<td>Triphenylacetoxysilane</td>
<td>(C₆H₅)₂SiOCH₃</td>
<td>91—92 (M.P.)</td>
<td>—</td>
<td>—</td>
<td>78,79</td>
</tr>
</tbody>
</table>

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Table 42

Properties of Mixtures of Certain Substituted Esters of Orthosilicic Acid with Alcohols (Bibl. 24, 80)

<table>
<thead>
<tr>
<th>Substituted Esters</th>
<th>Alcohol</th>
<th>B.P. of Mixture °C</th>
<th>Refr. Index nD°</th>
<th>Alcohol Content of Mixture, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH₃)₃SiOCH₃</td>
<td>CH₃OH</td>
<td>50</td>
<td>1.3637</td>
<td>14–16</td>
</tr>
<tr>
<td>(CH₃)₂SiOC₂H₄</td>
<td>C₂H₅OH</td>
<td>66</td>
<td>1.3729</td>
<td></td>
</tr>
<tr>
<td>(CH₃)₂SiOCH₂CH(CH₃)₂</td>
<td>(CH₃)₃CHCH₂OH</td>
<td>111</td>
<td>1.3963</td>
<td>40–44</td>
</tr>
</tbody>
</table>

Table 43

Physical Properties of Tri-Substituted Esters and Anhydrides of Orthosilicic Acid

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>B.P. °C</th>
<th>Spec. Grav. d₂⁰</th>
<th>Refr. Index nD°</th>
<th>Bibl.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trimethylmethoxysilane</td>
<td>(CH₃)₃SiOCH₃</td>
<td>57.2</td>
<td>—</td>
<td>1.3679</td>
<td>24</td>
</tr>
<tr>
<td>(CH₃)₂SiOC₂H₄</td>
<td>56.5–56.7 (747 mm)</td>
<td></td>
<td>1.3678</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>Trimehylbutoxysilane</td>
<td>(CH₃)₂SiOCH₃</td>
<td>75</td>
<td>0.7573</td>
<td>1.3741</td>
<td>10,24</td>
</tr>
<tr>
<td>(CH₃)₂SiOCH₃</td>
<td>123</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CH₃)₂SiOC₂H₄</td>
<td>124.6</td>
<td>0.7774</td>
<td>1.3825</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>Triethyl-2-chloroethoxysilane</td>
<td>(CH₃)₂SiOC₂H₄Cl</td>
<td>134.3</td>
<td>—</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triethylethoxysilane</td>
<td>(CH₃)₂SiOC₂H₄</td>
<td>131–132</td>
<td>0.9443</td>
<td>1.4140</td>
<td>30</td>
</tr>
<tr>
<td>(CH₃)₂SiOC₂H₄</td>
<td>123</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triethylacetoxysilane</td>
<td>(CH₃)₂SiOC₂H₄</td>
<td>131–132</td>
<td>0.8414</td>
<td>1.4140</td>
<td>3,71</td>
</tr>
<tr>
<td>(CH₃)₂SiOC₂H₄</td>
<td>153</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tripropylethoxysilane</td>
<td>(CH₃)₂SiOC₂H₄</td>
<td>154</td>
<td>0.8310 (26.5°)</td>
<td>1.4714</td>
<td>24</td>
</tr>
<tr>
<td>(CH₃)₂SiOC₂H₄</td>
<td>168</td>
<td></td>
<td>0.9039</td>
<td>—</td>
<td>3.4</td>
</tr>
<tr>
<td>Tripropylacetoxysilane</td>
<td>(CH₃)₂SiOC₂H₄</td>
<td>198–210</td>
<td>0.8657</td>
<td>1.4560</td>
<td>33</td>
</tr>
<tr>
<td>(CH₃)₂SiOC₂H₄</td>
<td>212–216</td>
<td></td>
<td></td>
<td>—</td>
<td>77</td>
</tr>
<tr>
<td>Triisopropylethoxysilane</td>
<td>(CH₃)₂SiOC₂H₄</td>
<td>—</td>
<td>0.8657</td>
<td>1.4560</td>
<td>33</td>
</tr>
<tr>
<td>Triphenylacetoxysilane</td>
<td>(CH₃)₃SiOCH₃</td>
<td>91–92</td>
<td>—</td>
<td>—</td>
<td>78.79</td>
</tr>
</tbody>
</table>

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difference between these two classes of compounds is most distinctly seen when we consider the reactions of hydrolysis.

**Hydrolysis**

The reaction of hydrolysis of the substituted esters of orthosilicic acid by water proceeds by a mechanism similar to that of the hydrolysis of esters of orthosilicic acid and of silicon tetrachloride (cf. page 83). The end product of the hydrolysis of esters of orthosilicic acid and of SiCl₄, however, is an inorganic polysiloxane, silica gel, while the products of the hydrolysis of substituted esters are polyorganosiloxanes.

The intermediate products of the hydrolysis and condensation of the substituted esters of orthosilicic acid were isolated and investigated by me (Bibl. 35) considerably earlier than the intermediate products of the hydrolysis and condensation of the esters of orthosilicic acid. In investigating the hydrolysis of the substituted esters, the mechanism of the high-molecular organosilicon compounds was established for the first time.

The velocity of the process of hydrolysis of substituted esters and of the condensation of the hydrolysis products depends not only on the factors that have been pointed out in our discussion of the process of hydrolysis of the esters of orthosilicic acid, but also on the structure, size, and number of the organic radicals bound to the silicon atom. The presence of radicals reduces the velocity of the hydrolysis of the alkoxyl groups and of the condensation of the hydrolysis products. This reduction is the greater, the larger the number of radicals, and the larger they are in size. The presence of large radicals, and also as branched radicals, exerts particularly great influence on the rate of hydrolysis and condensation; obviously, in the hydrolysis of substituted esters of this type, the steric factor plays a substantial role. The character of the hydrolysis product of a substituted ester is determined by the functionality of the system. As we have stated, the func-
tionality of an individual substitution product is defined as the number of reactive Si-OC bonds. The functionality of a mixture is a quantity intermediate between the functionalities of the individual components. For instance, the functionality of a mixture of 1 mol of diethyldiethoxysilane and 1 mol of triethylethoxysilane is 1.5.

In the general case the functionality of a system may be found from the formula:

\[ F = \frac{M + 2D + 3T + 4Q}{M + D + T + Q} \]

where \( M, D, T, \) and \( Q \) are the respective number of mols of mono-, bi-, tri-, and tetrafunctional components in the mixture.

The higher the functionality of the system, the higher the molecular weight of the hydrolysis products (for systems with the same organic radicals) and the more will it in structure and properties approach the hydrolysis product of the esters of orthosilicic acid, namely silica gel. The products of the hydrolysis of mixtures of low functionality (up to 2), however, are low-molecular liquids with physical properties having nothing in common with the products of the hydrolysis of esters of orthosilicic acid.

In studying the mechanism of formation of organosilicon polymers, that is, of the polyorganosiloxanes, the peculiarities characteristic for the processes of hydrolysis of compounds of different functionality must be borne in mind. For this reason we shall describe the processes of hydrolysis of substituted esters of varying functionality: monofunctional, bifunctional, trifunctional, and mixtures of various functionalities.

Hydrolysis of Systems with a Functionality Less than Two

Under the action of water on monofunctional substituted esters of orthosilicic acid, only the hexaalkyldisiloxane is formed:

\[ \begin{align*}
R_3\text{Si} & \text{HO} + \text{H}_{2}\text{O} & \rightarrow & R_3\text{Si} \text{OH} + \text{R}^{0}\text{OH} \\
2R_3\text{Si} \text{OH} & \rightarrow & R_3\text{SiOSiR}_3 + \text{H}_{2}\text{O}
\end{align*} \]
The intermediate products of hydrolysis, trialkylhydroxysilanes, can probably be isolated when the process is run in a weakly alkaline medium, but the literature describes only the preparation of trialkylhydroxysilanes from trialkyl-(aryl)-chlorosilanes, or from the salts, silanolates. The difficulty of preparing trialkylhydroxysilanes from substituted esters is obviously due to the fact that the presence of three organic radicals attached to the silicon atom considerably reduces the mobility of the alkoxy groups, so that the use of catalysts, acid in this case, are necessary for the conduct of the process of hydrolysis. The presence of acids sharply accelerates the process of condensation, so that the principal reaction product is a hexaalkylsiloxane.

The methyl radicals weaken the mobility of the alkoxy group to hydrolysis, but only to a minimum extent. The velocity of condensation of trimethylhydroxysilane is high, however, and on the hydrolysis of trimethylthioxysilanes by water in the presence of HCl or sulfuric acid, the reaction product is only hexamethyldisiloxane (Bibl.36).

The practical importance of monofunctional compounds is related to their use for ring-closure of polyorganosiloxanes. The process of preparing polymers in whose molecules the ends of the siloxane chains are closed by monofunctional groups, may be accomplished either by catalytic rearrangement of a mixture of hexaalkylsiloxanes and the hydrolysate of bifunctional compounds, or by the cohydrolysis of mixtures of monofunctional compounds with bi- and trifunctional compounds, that is, by hydrolysis of mixtures with an average functionality between one and two. By varying the ratio between the monofunctional compounds and compounds with a larger number of functional groups (up to tetrafunctional), liquid polysiloxanes with a longer or shorter siloxane chain, and having either linear or branched structure, may be obtained.

Polymers of linear structure are prepared by cohydrolysis of a mixture of trialkylalkoxysilanes and dialkyldialkoxyxilanes:
When the ratio between the mono- and bifunctional substituted esters is varied, the total functionality of the system may vary between 1 and 2. In this case, the average length of the siloxane chain of the compound formed will vary accordingly. It must be borne in mind that the hydrolysis of a mixture of two compounds of different functionality cannot be exactly reflected by any single chemical reaction, for instance that given above. In all cases, as a result of the process of hydrolysis, complex mixtures are formed containing linear compounds with siloxane chains of varying length. As the main reaction product, however, a polymer may be obtained in which the number of silicon atoms is determined by the ratio between the quantity of mono- and bifunctional compounds. The number of silicon atoms in the main compounds may be calculated. We make use of the following reasoning to set up the equation.

Let us imagine that a molecule of polymer \( R_2SiO(SiR_2O)_xSiR_2 \), obtained by the reaction given above, is divided into two equal parts. The number of bifunctional structural units in each part, equal to the ratio between the number of bi- and monofunctional structural units in the molecule, will be equal to the ratio between the number of mols of the bifunctional substituted ester and the number of mols of the monofunctional substituted ester, \( \frac{D}{M} \); the number of structural units in each part of the polymer, will obviously be one unit more than this ratio; while the total number of siloxane units in the polymer chain (the number of silicon atoms) will be:

\[
x = 2\left(\frac{D'}{M} + 1\right)
\]

where \( D = \) number of mols of difunctional substituted esters;

\( M = \) number of mols of monofunctional substituted ester.

In this case, the equation for calculating the average functionality of a system consisting of a mixture of mono- and bifunctional compounds, will take the following form:
By simultaneously solving eqs. (1) and (2), the relation between the number of units in the siloxane chain and the average functionality of the system can be found:

\[ \phi = \frac{M + 2D}{M + D} \quad \text{or} \quad \phi = \frac{1 + \frac{2D}{M}}{1 + \frac{D}{M}} \]  

(2)

For monofunctional compounds (\( \phi = 1 \)), the solution of the equation leads to the result that the number of silicon atoms in the chain must be equal to 2 - disiloxane is formed. When the functionality is increased, the average number of siloxane units in the chain also increases, and for \( \phi = 2 \), it is theoretically equal to infinity.

As stated above, in fact the actual product of the reaction is a polydisperse mixture, which also contains cyclic polymers, so that at a functionality of this system that is close to 2, the actual average length of the chain is found to be lower than the calculated value.

We present an example of the preparation of polymers of relatively low average molecular weight (Bibl.37).

**Hydrolysis of Mixtures of Functionality Less than Two.** 1. A mixture of 1393 g of dimethyl-diethoxysilane and 1110 g of trimethylethoxysilane (\( \phi = 1.5 \)) is treated for 1 hour, with stirring, with a solution of 7.5 g of NaOH in 254 g of water at a temperature of 40 - 65°C. Then 50 ml of water are added to the mixture, and it is heated under a reflux condenser at boiling point for 2 hours. The ethanol formed during the hydrolysis is then distilled off, up to a temperature of 100°C. The or-7rosilicon compounds entrained during this distillation are separated by washing the ethanol with water, and are returned to the main mass. The mixture of siloxanes, to complete the hydrolysis, is then treated at boiling point with 550 ml of 20% HCl. The reaction product (1425 g) is washed, dried, and rectified in a rectification
column (1.3 m high), packed with 6 x 0.6 mm glass spirals. During rectifications, a series of individual polymethylsiloxanes, of the general formula \( \text{CH}_3\text{Si}(\text{CH}_3)_2\text{O}_x\text{Si(CH}_3)_3 \), where \( x = 2, 3, 4, \) and 5, are separated.

The residue in the still after rectification amounts to only 10%, and its viscosity is low (12 centistokes).

Table 44 gives the properties of the products so obtained.

<table>
<thead>
<tr>
<th>( x + 1 )</th>
<th>( a) )</th>
<th>( b) )</th>
<th>( c) )</th>
<th>( d) )</th>
<th>( e) )</th>
<th>( f) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>152</td>
<td>-86</td>
<td>1.04</td>
<td>0.8182</td>
<td>1.3822</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>192</td>
<td>-76</td>
<td>1.53</td>
<td>0.8510</td>
<td>1.3870</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>-84</td>
<td>-</td>
<td>-</td>
<td>1.3902</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>-</td>
<td>-90</td>
<td>-</td>
<td>-</td>
<td>1.3922</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>-</td>
<td>-63</td>
<td>-</td>
<td>-</td>
<td>1.3882</td>
<td></td>
</tr>
</tbody>
</table>

a) Number of silicon atoms \( (x + 1) \); b) Boiling point, \( ^{\circ}\text{C} \); c) Melting point, \( ^{\circ}\text{C} \); d) Viscosity, centistokes; e) Specific gravity, \( d_{40}^{20} \); f) Refractive index, \( n_{D}^{20} \)

Entirely different products are obtained on the hydrolysis of mixtures of functionality close to two.

2. A mixture of 288.6 g of dimethyldiethoxysilane and 5.9 g of methyltriethoxysilane (Bibl. 37) (\( \Phi = 1.95 \)) is treated, under stirring, with a solution of 0.2 g of NaOH in 36 g of water for 30 minutes at 25 - 60\( ^{\circ}\text{C} \). The mixture is heated to 100\( ^{\circ}\text{C} \), and at the same time the ethanol formed (169 g) is distilled off. In order to complete the hydrolysis, 150 ml of 20\% HCl is then added to the mixture, and it is again heated to boiling. The reaction product is washed and dried over calcined CaCl\(_2\). On fractional distillation up to 250\( ^{\circ}\text{C} \), under a residual pressure of 1 mm, the retort residue amounts to 123.4 g (83\% of the weight of the product of hydrolysis). The
column (1.3 m high), packed with \(6 \times 0.6\) mm glass spirals. During rectifications, a series of individual polymethylsiloxanes, of the general formula \(\text{CH}_3[\text{Si(\text{CH}_3)_2}]_x\text{Si(\text{CH}_3)_3}\), where \(x = 2, 3, 4,\) and \(5\), are separated.

The residue in the still after rectification amounts to only 10\%, and its viscosity is low (12 centistokes).

Table 44 gives the properties of the products so obtained.

**Table 44**

**Physical Properties of Linear Polymethylsiloxanes \(\text{CH}_3[\text{Si(\text{CH}_3)_2}]_x\text{Si(\text{CH}_3)_3}\)**

<table>
<thead>
<tr>
<th>(x+1)</th>
<th>(a))</th>
<th>(b))</th>
<th>(c))</th>
<th>(d))</th>
<th>(e))</th>
<th>(f))</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>152</td>
<td>-86</td>
<td>1.64</td>
<td>0.8182</td>
<td>1.3982</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>192</td>
<td>-76</td>
<td>1.53</td>
<td>0.8510</td>
<td>1.3977</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>-84</td>
<td>-</td>
<td>-</td>
<td>1.3982</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.3982</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.3982</td>
<td></td>
</tr>
</tbody>
</table>

\(a)\) Number of silicon atoms \((x + 1)\); \(b)\) Boiling point, °C; \(c)\) Melting point, °C; \(d)\) Viscosity, centistokes; \(e)\) Specific gravity, \(d_{20}^\circ\); \(f)\) Refractive index, \(n_{20}^D\)

Entirely different products are obtained on the hydrolysis of mixtures of functionality close to two.

2. A mixture of 288.6 g of dimethyldiethoxysilane and 5.9 g of methyltriethoxysilane (Pibl.37) \((\Phi = 1.95)\) is treated, under stirring, with a solution of 0.2 g of NaOH in 36 g of water for 30 minutes at 25 - 60°C. The mixture is heated to 100°C, and at the same time the ethanol formed (169 g) is distilled off. In order to complete the hydrolysis, 150 ml of 20% HCl is then added to the mixture, and it is again heated to boiling. The reaction product is washed and dried over calcined CaCl\(_2\). On fractional distillation up to 250°C, under a residual pressure of 1 mm, the retort residue amounts to 123.4 g (83% of the weight of the product of hydrolysis). The
viscosity of the retort residue is 81 centistokes.

The above examples illustrates the possibility of preparing organosilicon polymers with predetermined physical properties: viscosity, boiling point, etc, by varying the functionality of the system. The reactions we have given above allow preparation of liquid organosilicon polymers containing various organic radicals and possessing various degrees of viscosity.

Systems with a functionality of less than two may be not only mixtures of monofunctional and difunctional compounds, but also mixtures of monofunctional and trifunctional compounds, and even of monofunctional and tetrafunctional compounds with the former predominant. The products of hydrolysis and polycondensation of such mixtures are polysiloxanes of branched structure, which as a rule have very low freezing points. Thus, for instance, it has been proposed to prepare liquids by cohydrolysis of dimethylphenylethoxysilane and methyltriethoxysilane (Bibl.38). The reaction products are liquid polyorganosiloxanes, whose molecules have a side chain in each structural unit:

\[
RR_2'^6S(O)\Bigg[\begin{array}{c}
R' \\
- Si - O \\
| OSiRR_2' \\
\end{array}\Bigg]-5RR_2
\]

In the case where there are not only monofunctional and trifunctional monomers in the mixture, but also bifunctional monomers, the polysiloxanes formed do not have a side chain in each unit of the chain.

On the cohydrolysis of an ester of orthosilicic acid with considerable quantities of monofunctional compounds (functionality of the mixture less than two) in the presence of an acid or alkali, a series of compounds of the general formula \( Si[OSi(CH_3)_2R]_4 \), have been prepared, whose properties are given in Table 45. The products of hydrolysis, together with such compounds, also contain hexaalkyldisiloxanes and polymers of the general formula.
From the data given in a patent (Bibl.39), the compound so formed contains up to 40 silicon atoms in the chain. They possess a very low vapor pressure, up to 0.1 mm at 300°C.

Table 45

Physical Properties of Certain Tetraalkylsiloxysilanes Si[OSi(CH₃)₂R]₄

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c)</th>
<th>d)</th>
<th>e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>91 (9 mm)</td>
<td>-53</td>
<td>0.875</td>
<td>1.3865</td>
</tr>
<tr>
<td>C₂H₅</td>
<td>102 (2 mm)</td>
<td>-45</td>
<td>0.895</td>
<td>1.4112</td>
</tr>
<tr>
<td>C₆H₅</td>
<td>222 (5 mm)</td>
<td>-62</td>
<td>1.049</td>
<td>1.5178</td>
</tr>
</tbody>
</table>

a) Radical R; b) Boiling point, °C; c) Melting point, °C; d) Specific gravity, d₂₀; e) Refractive index, n₂₀

The most substantial element in the conduct of the hydrolysis of a mixture of different organosilicon compounds is the finding of the optimum conditions under which actual cohydrolysis takes place, and the reaction product contains structural units of different monomers in a single molecule. If the rate of hydrolysis and condensation of the different compounds making up the mixture are approximately the same, the conduct of the cohydrolysis involves no difficulty. If, however, these velocities differ sharply under the reaction conditions, then the product of the hydrolysis and condensation is not a copolymer, but merely a mechanical mixture of different polymers which does not possess the properties inherent in a copolymer. The finding of the optimum reaction conditions under which cohydrolysis takes place is therefore an important and sometimes a complicated problem.
Hydrolysis of Bifunctional Compounds and Mixtures

While a chemical formula that rather accurately reflects the possible processes can be written for the reaction of hydrolysis and condensation of the hydrolysis products of monofunctional substituted esters of orthosilicic acid, the reaction of water with the dialkyldialkoxy silanes proceeds in a manner considerably more complicated.

A detailed study of the mechanism of the reactions made by me (Bibl. 40) has allowed me to establish that the process of hydrolysis is accompanied by condensation of the hydroxy derivatives to form high-molecular polydialkylsiloxanes.

On addition of an insignificant quantity of water to a dialkyldialkoxy siloxane, hydrolysis of one of the alkoxy groups takes place:

\[ R_2Si(OR')_2 + H_2O \rightarrow R_2Si(OR')OH + R'O\]

followed by the condensation of the hydrolysis products.

\[ 2R_2Si(OR')OH \rightarrow R_4Si(OSiR_2(OR'))_2 + H_2O \]

When more water is added, the hydrolysis and condensation continue, according to the reaction:

\[ R_2Si(OR')OSiR_2(OR') + H_2O \rightarrow R_4Si(OSiR_2(OR'))_2 + H_2O \]

Thus the intermediate products of hydrolysis and condensation are linear polydialkylsiloxanes with alkoxy groups at the ends, having the general formula

R'O(SiR₂O)_xR.

Hydrolysis of Diethyldiethoxysilane. To 44 g of diethyldiethoxysilane, under stirring, 16.9 g of 80% ethanol is added (0.75 mol of water per mol of substituted ester). The mixture is kept in a thermostat at 90°C for 10 hours, after which the ethyl alcohol is distilled off, and the mixture is fractionated at reduced pressure. The principal reaction product is octaethyldioxytetrasiloxane, but there are al-
ways a number of compounds of the homologous polymer series \( \text{C}_2\text{H}_5\text{O}[\text{Si}(\text{C}_2\text{H}_5)_2\text{O}]\text{C}_2\text{H} \)

present in the mixture.

When various quantities of water are used, we have isolated, as the principal reaction products, the compounds shown in Table 46.

Figure 20 shows the velocity of hydrolysis.

Table 46

<table>
<thead>
<tr>
<th>Characteristics of Separated Diethoxypolydiethylsiloxanes</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_2\text{H}_5\text{O}[\text{Si}(\text{C}_2\text{H}_5)_2\text{O}]\text{C}_2\text{H} )</td>
</tr>
<tr>
<td>a</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>0.75</td>
</tr>
<tr>
<td>0.85</td>
</tr>
<tr>
<td>0.87</td>
</tr>
<tr>
<td>0.90</td>
</tr>
</tbody>
</table>

a) Number of mols of water per mol of diethyldiethoxysilane; b) Number of silicon atoms in siloxane chain, \( X \); c) Boiling point, \( ^\circ\text{C} \); d) Ethoxyl value, \%.

The length of the chain of the principal reaction product — the average chain length — depends on the quantity of water introduced into the reaction, and can be calculated mathematically (Bibl.41).

Let us adopt the following notation:

\( N \) = number of mols of product being hydrolysed;

\( N_1 \) = number of mols of water introduced into the system, equal to the number of siloxane bonds formed.

As a result of the hydrolysis reaction, the number of mols of organosilicon compound decreases, and will be equal to the difference

\[ N - N_1 \]

The average number of silicon atoms in the siloxane chain formed will be equal to the ratio of the number of molecules before hydrolysis to the number of molecules
after hydrolysis, that is

\[ x = \frac{\frac{N}{N-N_1}} \]

By dividing the numerator and denominator by \( N \), and denoting the expression \( \frac{N_1}{N} \) by \( n_b \), we get:

\[ x = \frac{1}{1-n_b} \]

where \( n_b \) represents the molar weight of the water taken in the reaction of hydrolysis. This equation, as has been indicated, has been introduced for the ideal case, that is, for infinitely small velocity of introduction of water and for its uniform distribution. It has been found in practice that this equation is correct for systems with a ratio of up to 0.9 mol of water per mol of organosilicon compound. When larger quantities of water are used, there is a discrepancy between the calculated and experimental data, which is due to the nonuniform course of the reaction in the different zones, as well as to the formation of a certain quantity of cyclical siloxanes together with the linear siloxanes.

A study of the principal fractions separated by fractionation under high vacuum has shown that in hydrolysis with small quantities of water, the products are colorless viscous liquids. Their viscosity increases with the degree of condensation of the product. All of them are readily soluble in benzene, alcohol, acetone, toluene, alcohol-benzene mixtures, and other organic solvents.

On repeated distillation of the principal fractions, even after six-fold fractionation, no break in the continuity of the boiling points is observed. The products do not crystallize on cooling, but solidify slowly, and are converted into
glasslike substances, which indicates the probable presence of insignificant quantities of homologs, which hinder the process of crystallization.

The molecules of the compound so prepared have an open chain. A proof of this is the good correspondence between the numbers of the ethoxyl groups, confirming the presence of two ethoxyl groups in the molecule. Linear polymers are formed as a result of the step-wise hydrolysis of triethyldiethoxysilane in a neutral medium with insufficient water (Bibl.41).

With an excess of water and in the presence of HCl, not only linear but also cyclic polymers are obtained. Thus, for example, the hydrolysis of diethyldiethoxysilane by dilute HCl leads to the formation of liquid products. Repeated fractionation under reduced pressure separated two main fractions with respective boiling points (8 mm) of 150 - 200°C and 200 - 216°C.

The liquid of boiling point 150 - 200°C (8 mm), according to the analytical results, has the following elementary composition: Si 25.1%; C 48.9%; H 7.4%. The average molecular weight of the liquid is 530 and its refractive index $n_D^{15} = 1.439$.

It may be supposed that as a result of hydrolysis in an acid medium a compound with the formula $[(C_2H_5)_2SiO_x]$ is formed.

If we start out from this formula, the liquid should have the following elementary composition: Si 27.4%; C 47.1%; H 9.8%; O 15.7%.

The molecular weight of a unit of the chain, $(C_2H_5)_2SiO$ is 102, whence $x = 530: 102 = 5$.

Thus the main part of the substance of molecular weight 530 is apparently of the following structure*:

* The molecular weight of the pure substance corresponding to these formulas should be respectively 510 and 816.
The excess of oxygen by comparison with the calculated amount is probably due to the presence of insignificant admixtures of linear polymers with hydroxyl groups:

\[
\text{HO-Si} - \frac{\text{Si} \left( \text{C}_2\text{H}_5 \right)_x}{\text{Si}\left(\text{C}_2\text{H}_5\right)_2}
\]

in the liquid, together with the cyclic polymers.

The liquid of boiling point 200 - 216°C has the following elementary composition: Si 26.3% C 46%; H 9.7%; O 18.0%.

The average molecular weight of this liquid is 892, and its refractive index \(n_\text{D} = 1.441\).

It may be supposed, from the data of the analysis, that this compound likewise corresponds to the formula \([\left(\text{C}_2\text{H}_5\right)_2\text{SiO}]_x\), where \(x = 892 : 102 = 8\).

The postulated structure of the principal part of the substance* of molecular weight 892 is as follows:

\[
\text{Si}(\text{C}_2\text{H}_5)_2-\text{O} \rightarrow \text{Si}(\text{C}_2\text{H}_5)_2-\text{O} \rightarrow \text{Si}(\text{C}_2\text{H}_5)_2-\text{O} \rightarrow \text{Si}(\text{C}_2\text{H}_5)_2
\]

Besides this the substance probably also has admixtures of linear polymers containing hydroxyl groups:

* The molecular weight of the pure substance corresponding to these formulas should be respectively 510 and 816.
As indicated above, the product of the hydrolysis of alkylalkoxysilane is always a polydisperse mixture of polyalkylsiloxanes. The composition of the polydisperse mixture may be calculated under the conditions of the equal activity of the alkoxy groups attached to the silicon atoms, and of the absence of cyclic polymers. Both these conditions are satisfied in systems with an average degree of polymerization of about 10, which is obtained when 0.9 mol of water to 1 mol of dialkyldiethoxysilane is present in the system.

The distribution of the polymer homologs for such mixtures may be calculated from the statistical equation (Bibl.42):

\[ n_x = n_b^{x-1}(1 - n_b) \]

where \( n_x \) = molar proportion of polysiloxanes of degree of polymerization \( x \) (where \( x \) is the number of silicon atom in the polysiloxane chain of the molecules);

\( n_b \) = molar proportion of water taken for hydrolysis.

The hydrolysis of dimethyldiethoxysilane (Bibl.43) proceeds completely according to the reaction considered above on the example of diethyldiethoxysilane. When dimethyldiethoxysilane reacts with the quantity of water sufficient for complete hydrolysis, the reaction product consists of linear polydimethylsiloxanes with ethoxy groups at the ends of the molecules \( \left(C_2H_5O[Si(CH_3)_2O]_xC_2H_5\right) \). Individual products containing up to 11 silicon atoms in the molecule have been isolated and studied (Table 47).

**Hydrolysis of dimethyldiethoxysilane (Bibl.43).** 3051 g (54.4 mol) of dimethyldiethoxysilane, a solution of 21.8 g of NaOH in 733 ml (10.7 mol) of water is added over a period of 2 hours with stirring, and at a temperature up to 70°C. The
mixture is then held at the boiling point for an hour and is then heated to 100°C, simultaneously distilling off the ethanol formed. The reaction product is neutralized by passing carbon dioxide gas for 1.5 hours, and the precipitate is filtered off. The volatile polysiloxanes are distilled off, up to 150°C, under a residual pressure of 1 mm (retort residue 28.2%, viscosity of that residue 7.4 stokes) and are then rectified in a column 1.3 m high packed with 6 mm spirals. On rectification, the polydimethylsiloxanes whose properties are presented in Table 47 are separated.

Table 47

Physical Properties of Polydimethylsiloxanes of the General Formula

\[ \text{C}_2\text{H}_5[\text{Si(CH}_3)_2\text{O}]_x\text{C}_2\text{H}_5 \]

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c)</th>
<th>d)</th>
<th>e)</th>
<th>f)</th>
<th>g)</th>
<th>h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>114</td>
<td>-82</td>
<td>0.70</td>
<td>0.9305</td>
<td>1.3805</td>
<td>10.89</td>
<td>389</td>
</tr>
<tr>
<td>2</td>
<td>161</td>
<td>-134</td>
<td>0.06</td>
<td>0.8788</td>
<td>1.3860</td>
<td>50.12</td>
<td>532</td>
</tr>
<tr>
<td>3</td>
<td>196</td>
<td>-126</td>
<td>1.35</td>
<td>0.9024</td>
<td>1.3922</td>
<td>78.14</td>
<td>687</td>
</tr>
<tr>
<td>4</td>
<td>227</td>
<td>-124</td>
<td>1.78</td>
<td>0.9157</td>
<td>1.9350</td>
<td>96.87</td>
<td>850</td>
</tr>
<tr>
<td>5</td>
<td>257</td>
<td>-123</td>
<td>2.24</td>
<td>0.9207</td>
<td>1.3860</td>
<td>115.98</td>
<td>1120</td>
</tr>
<tr>
<td>6</td>
<td>274</td>
<td>-118</td>
<td>2.75</td>
<td>0.9317</td>
<td>1.3960</td>
<td>134.19</td>
<td>1170</td>
</tr>
<tr>
<td>7</td>
<td>292</td>
<td>-112</td>
<td>3.28</td>
<td>0.9364</td>
<td>1.3961</td>
<td>152.92</td>
<td>1330</td>
</tr>
<tr>
<td>8</td>
<td>311</td>
<td>-110</td>
<td>3.86</td>
<td>0.9406</td>
<td>1.3992</td>
<td>171.44</td>
<td>1580</td>
</tr>
<tr>
<td>9</td>
<td>-</td>
<td>-53</td>
<td>4.50</td>
<td>0.9442</td>
<td>1.4002</td>
<td>190.14</td>
<td>1680</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>-100</td>
<td>5.17</td>
<td>0.9471</td>
<td>1.4009</td>
<td>209.13</td>
<td>1810</td>
</tr>
<tr>
<td>11</td>
<td>-</td>
<td>-</td>
<td>5.89</td>
<td>0.9495</td>
<td>1.4012</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

a) Number of silicon atoms, X; b) Boiling point, °C; c) Melting point, °C; d) Viscosity at 25°C, poises; e) Specific gravity, \(d_4^{20}\); f) Refractive index, \(n_20\); g) Molar refraction; h) Parachor

Figure 21 shows the curve of distribution of the polymer homologs. It has a distinct maximum at four silicon atoms in the chain. This indicates that the principal reaction product is octamethyldiethoxytetrasiloxane. This result is in complete agreement with the calculation by the formula given above:

\[ X = \frac{1}{1 - n_b} = \frac{1}{40.7} \approx 4 \]
Other polymer homologs are obtained in the statistical quantities; and together with them, a certain amount of the cyclic products of complete hydrolysis is also formed: octamethylcyclotetrasiloxane and decamethylcyclopentasiloxane. The presence of other cyclic compounds in the hydrolysis product has not been established.

![Graph](image)

**Fig. 21** - Distribution of Polymer Homologs Formed on the Hydrolysis of Dimethyldiethoxysilane:

1. \( C_2H_5O[Si(CH_3)_2O]_x C_2H_5 \)
2. \([Si(CH_3)_2O]_x\)

a) Number of silicon atoms in the polysiloxanes formed; b) Content of polysiloxanes, mol %

**Fig. 22** - Relation between Rate of Hydrolysis of Ethoxysilanes and their Functionality:

1. \( C_2H_5Si(OCC_2H_5)_3 \)
2. \((C_2H_5)_2Si(OCC_2H_5)_2\)
3. \(Si(OCC_2H_5)_4\)

a) Time, hours; b) Number of hydrolyzed ethoxy groups, %

Figure 22 shows the effect of the variation of the functionality of the system on the rate of hydrolysis (Bibl. 41, 44) of ethoxysiloxanes.

Under the action of an excess of water in the alcoholic solution, the hydrolysis of tetraethoxysilane and ethyltrioethoxysilane proceeds more than 90% to completion in 1 hour at 60°C (curves 1 and 3), while diethyldeethoxysilane (curve 2) at 90°C is 98% hydrolyzed only after 6 hours of heating (Bibl. 41).

The statistical distribution of polymer homologs in the polydisperse mixture of the partial hydrolyzates of bifunctional compounds is an experimental confirmation.
of the view that the velocity of cleavage of alkoxy groups is independent of the
length of the siloxane unit of the polymer. The difficulty of hydrolytic cleavage of the
residual alkoxy groups does not contradict this circumstance, since the primary factor
responsible for the lowering of the rate of hydrolysis in this case is the reduction in
the concentration of the alkoxy groups. In addition, the increase in the viscosity of
the polymer is a substantial factor.

It is interesting to note the presence of a second organic radical in the original
product has less of an effect on the velocity of the condensation reaction than on the
velocity of hydrolysis. For this reason, in contrast to the trifunctional compounds, the
velocity of the process of condensation of the hydrolysis products of bifunctional com-
pounds shows almost no lag behind the velocity of the process of their hydrolysis.

A study of the effect of the quantity of water introduced into the reaction on the
properties of the polymer obtained (Bibl. 43) has shown that with increasing quantity of
water so introduced, the quantity of the undistilled fraction (Fig. 23) increases, and
the number of ethoxy groups decreases in both distilled and undistilled fractions
(Fig. 24). As a result of a deeper completion of the hydrolysis reaction, the molec-

Fig. 23 - Influence of the Quantity of Water Taken for the Hydrolysis of Dimethyldiethoxysilane on the Viscosity of the Hydrolysis Products and on the Percentage Content of the Volatile Part in the Hydrolysis Product:
1 - Viscosity of hydrolysis product; 2 - Viscosity of nonvolatile part of hydrolysis product; 3 - Viscosity of volatile part of hydrolysis product; 4 - Percentage content of the volatile part
a) number of mols of water per mol of \((\text{CH}_3)_2\text{Si(OC}_2\text{H}_3)_2\); b) Viscosity at 25°C, centistokes; c) Content of volatile part, %
ular weight of the retort residue increases (Fig. 24), and also its density and its refractive index (Fig. 25).

**Hydrolysis of Dimethyldiethoxysilane by Various Quantities of Water.** To 8051 g of dimethyldiethoxysilane, with stirring, at a temperature of 70°C, a solution of 21.8 g of NaOH in 882 g of water is added over a period of 1 hour (0.9 mol of water per mol of dimethyldiethoxysilane). The mixture is heated to boiling for 1 hour; the volatile products up to 125°C are distilled off, and from these parts the ethyl alcohol is washed away by water, while the organosilicon compounds are returned to the main mass of polymers.

A first sample is now taken, after which an additional quantity of water is added to the mixture, in order to bring up the ratio \( \frac{H_2O}{Si} \) to 0.921; the process of hydrolysis is now repeated, then a second sample is taken, water is again added, and so on. In this way a series of samples are obtained, representing the various products of the hydrolysis of dimethyldiethoxysilane by water at ratios from 0.9 to 1.072 mol of water per mol of dimethyldiethoxysilane. All the samples so obtained were distilled under reduced pressure, and the physical and chemical characteristics of the distilled and undistilled fractions were studied.

**Preparation of Organosilicon Liquids by the Method of Hydrolysis of Dialkyldiethoxysilanes.**

Organosilicon polymeric liquids are prepared from dialkyldiethoxysilanes by the action of an excess of water on them (usually in the presence of an acid as a catalyst). After completion of the reaction, cyclic dialkylsiloxanes are formed:

\[ xR_2Si(OR')_2 + xH_2O \rightarrow (R_2SiO)_x + 2xR'OH \]

On the action of dilute HCl on diethylidioxysilanelate (Bibl. 44), a mixture of polydiethylsiloxanes is formed, containing a series of cyclic diethylsiloxanes, mainly pentacyclosiloxane \([Si(C_2H_5)_2O]_5\) and octacyclosiloxane \([Si(C_2H_5)_2O]_8\). The cyclic diethylsiloxanes are low-polar substances; this is confirmed by the fact that
their dielectric constant is close to the square of the refractive index.

The complete hydrolysis of dimethyl disthoxysilane may be effected (Bibl.45) by heating it with a mixture, in equal volume, of 95% ethanol and concentrated HCl (1:1) at boiling point for 4 - 8 hours. The reaction product is washed, dried under reduced pressure at 120°C, and the volatile dimethylsiloxanes are then distilled off up to 250°C (4 mm). The mixture distilled off is again treated with 20% HCl at boiling point, washed, dried, and rectified. Individual cyclic dimethylsiloxanes \([Si(CH_3)_2O]_x\) are obtained, with chains containing up to 12 silicon atoms. Table 48 gives the physical properties of the polysiloxanes so prepared.

Table 48

Physical Properties of Cyclic Dimethylsiloxanes of the General Formula \([Si(CH_3)_2O]_x\)

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c)</th>
<th>d)</th>
<th>e)</th>
<th>f)</th>
<th>g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(x)</td>
<td>Number of silicon atoms</td>
<td>Melting point, °C</td>
<td>Boiling point, °C</td>
<td>Viscosity (at 25°C)</td>
<td>Specific gravity, (d_4^{25})</td>
<td>Refractive index, (n_D^{25})</td>
</tr>
<tr>
<td>4</td>
<td>17.5</td>
<td>175.74 (20 mm)</td>
<td>14.87</td>
<td>0.9555 (20°)</td>
<td>1.3968 (20°)</td>
<td>77</td>
</tr>
<tr>
<td>5</td>
<td>44</td>
<td>204.5</td>
<td>14.87</td>
<td>0.9531</td>
<td>1.3948</td>
<td>77</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>125 (21 mm)</td>
<td>14.47</td>
<td>0.9613</td>
<td>1.3996</td>
<td>77</td>
</tr>
<tr>
<td>7</td>
<td>32</td>
<td>148 (20 mm)</td>
<td>14.23</td>
<td>0.9664</td>
<td>1.4118</td>
<td>109</td>
</tr>
<tr>
<td>8</td>
<td>90</td>
<td>130 (1 mm)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>130 (1 mm)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>150 (1 mm)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>160 (1 mm)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>180 (1 mm)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

a) Number of silicon atoms, \(x\); b) Melting point, °C; c) Boiling point, °C; d) Viscosity (at 25°C) centistokes; e) Specific gravity, \(d_4^{25}\); f) Refractive index, \(n_D^{25}\); g) Flash point, °C

The preparation of high-boiling products of relatively high molecular weight, which possess a number of valuable properties, is of greater practical interest. This may be accomplished by thermal or catalytic treatment of the hydrolysis products. (cf. page 742 et seq).

A considerably more convenient method of preparing polysiloxane liquids from
dialkyldialkoxydimethyldiethoxydimethyldiethoxysilanes is hydrolysis in the presence of sulfuric acid. In this case, the process of hydrolysis is combined with catalytic rearrangement, and the byproducts, the low-molecular polyorganosiloxanes, are formed in minimum amounts (cf. page 742 ff.).

Method of Preparing Liquid Polymers (Bibl.46). 1. A mixture of two parts of dimethyldioxydimethyldiethoxysilane, 1 part of 95% of ethanol, and 1 part of concentrated hydrochloric acid, is boiled for an hour. The hydrolysis product at 30°C has a viscosity of 45 centistokes, a flash point of 118°C, and an average molecular weight of 1100. On heating the product in the retort of a rectification column in a current of carbon dioxide gas at 245°C, its viscosity increases to 75 centistokes, its flash point to 244°C, and its molecular weight to 1500.

2. Dimethyldioxydimethyldiethoxysilane is mixed with 85% sulfuric acid (34% by volume) for 5 minutes. The reaction product is a mixture of polymethylsilsiloxanes (of viscosity 158 centistokes). We note that this method of hydrolysis is applicable not only to dialkyldialkoxydimethyldiethoxysilanes, but also to all mixtures of substituted esters the functionality of whose mixtures is not over two.

The viscosity and other physical properties of the products depends on the reaction conditions, time of treatment, temperature, etc. Thus, for example, in the
example given above on page 361, when the time of treatment is increased (Bibl.47), a polymer of molecular weight 15,000 can be obtained.

The polyorganosiloxane liquids have a small temperature coefficient of viscosity and an insignificant tangent of the dielectric loss angle (0.005). To obtain the polysiloxane liquid, it is by no means obligatory to use individual dialkyldialkoxy-
silanes or mixtures of pure substituted esters. One of the important methods of preparing such liquids is, for instance, the hydrolysis of a mixture obtained on alkylation of tetraethoxysilane by organomagnesium compounds.

A mixture of ethylethoxysilanes obtained by reacting 183 g of tetraethoxysilane, 55 g of magnesium, and 24.2 g of ethyl bromide dissolved in 550 ml of ethyl ether is hydrolyzed by pouring it into 1 liter of 25% sulfuric acid. As a result of the hydrolysis, polydiethoxysiloxanes are formed.

On the hydrolysis of a bifunctional mixture consisting of different compounds, it is necessary to assure reaction conditions under which cohydrolysis shall take place, and a mechanical mixture of polymers shall not be obtained. For this purpose it must be so selected as to bring the velocity of the reaction of the hydrolysis of the monomers in the composition of the mixture to be hydrolyzed close to the velocities of the condensation of the product of hydrolysis.

The cohydrolysis of dimethyldiethoxysilane and methylbenzyldiethoxysilane is conducted at an elevated temperature.
Cohydrolysis of Methylbenzylidethoxysilane and Dimethylidethoxysilane (Bibl.48).

To a mixture of 224 g of methylbenzylidethoxysilane and 296 g of dimethylidethoxysilane, 1395 ml of 95% ethanol containing a few drops of concentrated HCl is added, followed by 25 ml of water. The mixture is heated at 70°C for 4 hours. On the completion of the reaction, the solvent is distilled off, and the residue (a viscous liquid) is heated for 48 hours at 190°C, forming a waxy polymer.

The effect of the method of conducting the hydrolysis on the properties of the end product will be seen from the following experiment (Bibl.49).

A mixture of 90 g of dimethylidethoxysilane and 10 g of methyltriethoxysilane is boiled 4 hours with an equal volume of a mixture of ethyl alcohol and concentrated HCl (1:1). After completion of the hydrolysis, 10 g of trimethylethoxysilane is added dropwise to the mixture, and it is again boiled for an hour. The reaction product is washed with water, and the volatile compounds, (up to 230°C), are distilled off. The liquid so obtained has a viscosity of 45.5 centistokes at 25°C. Gelation takes place only after heating for 256 hours at 200°C. If a mixture of all three of the above substituted esters is subjected to hydrolysis at once, under the same conditions and in the same proportions, the viscosity of the reaction product is only 21.9 centistokes, and the time of gelation on heating to 200°C is 63 hours.

On the hydrolysis of dimethylidethoxysilane in an acid medium with an excess of water, a liquid mixture of polymers is obtained, and is separated by distillation in a vacuum at 250°C into a nonvolatile part (amounting to 70 - 80%) and a low-polymer volatile part (amounting to 20 - 30%). The low polymer part is mainly a mixture of cyclic polydimethylsiloxanes with 4 to 8 silicon atoms in the ring. Cyclic polymers are prepared in considerably better yield on the thermal cleavage of high-polymeric dimethylsiloxane, which is effected by heating the polymer in a vacuum at 400°C in the presence of a small amount of NaOH and a catalyst (Bibl.49). Under these conditions, up to 90% of cyclic compounds are formed. The boiling points of the cyclic compounds increase regularly with their molecular weight. The freezing point of the
cyclic polymers fluctuates markedly and does not depend on the molecular weight. Thus, for example, the cyclic pentamer and heptamer crystallize with difficulty and have low melting points, while the trimer and tetramer have higher melting points, which evidently indicates that their structure is more symmetrical.

**Hydrolysis of Compounds and Mixtures of Functionalities Higher than Two**

The structure of the compounds formed on the hydrolysis and condensation of mixtures with a functionality over two is very sharply increased in complexity. The presence of trifunctional compounds, in the absence of an excess of monofunctional compounds, makes it possible for the polymer chains to be cross-linked by siloxane bridges.

\[
\begin{array}{ccc}
R & R & R \\
\vdots & \vdots & \vdots \\
\Sigma-Si-O-Si-O-Si & R & R \\
\Sigma-Si-O-Si-O-Si & R & R \\
\end{array}
\]

Thus on the hydrolysis of mixtures whose functionality is higher than two, polymers of network, (cross-linked) or three-dimensional structure are formed, which, as is well known, are characteristic for resins.

The most important parameters determining the properties of the hydrolysis product are the functionality of the system, and the size and nature of the organic radicals attached to the silicon atom.

If the functionality of the system is close to two, that is, if the number of trifunctional structural units is relatively small, the number of siloxane bridges cross-linking the polymer chains may prove to be insufficient to form a resinous polymer (Bibl. 50).

**Method of Preparing Polymethylsiloxane Liquids.** A mixture of 0.9 mol of dimethyldiethoxysilane and 0.1 mol of methyltriethoxysilane is hydrolyzed by treatment
with 1 N HCl at a temperature not over 45°C. The reaction product has a viscosity of 13 centistokes (contains ethoxyl groups); to intensify the hydrolytic process, it is heated in a stream of carbon dioxide gas; this increases the viscosity of the polymer to 29 centistokes, and then, to complete the hydrolysis, the product is boiled in a mixture of ethanol and concentrated HCl (1:1). This leads to an increase in viscosity to 82 centistokes.

Liquids of the above type have a low freezing point and a low temperature coefficient of viscosity. For instance, the polyorganosiloxane obtained by co-hydrolysis of 90 parts of dimethylethoxysilane and 10 parts of methyltristethoxysilane under the conditions described has a freezing point of -78°C; its viscosity at 100°C is 12 centistokes, and at -40°C is 510 centistokes (for mineral oil at the same temperatures, it is 7 and 13,300 centistokes respectively).

In spite of the presence of trifunctional structural units in the polymer, it is relatively stable and does not gel at a temperature of 100°C over a period of 600 hours, and can therefore be used as a low-temperature liquid in hydraulic instruments.

The value of the functionality of the system at which the product of hydrolysis acquires the properties of a resinous polymer strongly depends on the size and structure of the organic radical. The maximum allowable value of the functionality of the system does not exceed 2.1 for the preparation of liquid polymers in the above examples, and it is not possible to obtain a resinous polymer for polyethoxysiloxanes with a functionality of 2.4 (even on prolonged condensation of the hydrolysis products (Bibl.51). Systems with still higher functionality, containing higher radicals, yield only liquid polymeric products of hydrolysis (the polybutoxysiloxanes above discussed (Bibl.52) may be cited as an example, for they still remain liquid.
at a functionality of the system running up to 2.6).

The most convenient method of investigating the process of hydrolysis and condensation of trifunctional monomers is their partial hydrolysis under the action of an insufficient quantity of water. This method of investigation was used by me in 1938 (Bibl.35). It allowed me, for the first time, to establish, from the example of ethyl- and butyltriethoxysilanes, the mechanism of the reaction of the hydrolysis and condensation of trifunctional organo-silicon compounds. When water (in the amount of 0.5 mols) acts on alkyltriethoxysilanes, the main reaction product is disiloxane:

\[ \text{RSi(OR)}_3 + \text{H}_2\text{O} \rightarrow \text{RSi(OR)}_2\text{OH} + \text{R'OH} \]

\[ 2\text{RSi(OR)}_3\text{OH} \rightarrow \text{RSi(OR)}_2\text{OSi(OR)}_2\text{Si(OH)}_2 \]

**Partial Hydrolysis of Alkyltriethoxysilanes.** With 22.5 g of 90% alcohol, 48 g of ethyltriethoxysilane is mixed; the mixture is heated, with stirring, for 10 hours.

The main reaction product is diethyltetraethoxydisiloxane. On hydrolysis of isobutyltriethoxysilane, 44 g, in 18 g of 90% ethyl alcohol under similar conditions, the principal reaction product is diisobutyltetraethoxydisiloxane.

On the action of larger quantities of water, the process of hydrolysis continues further:

\[ \text{RSi(OR)}_3\text{OSi(OR)}_2 + \text{H}_2\text{O} \rightarrow \text{RSi(OR)}_2\text{OSi(OR)}_2\text{OH} + \text{R'O} \]

\[ \text{R'O} + \text{RSi(OR)}_2\text{OSi(OR)}_2\text{Si(OH)}_2 + \text{H}_2\text{O} \text{ etc.} \]
Ultimately, compounds of the general formula:

$$R'O[R'Si(OR')_x]R'$$

are formed.

Thus, when 48 g of ethyltriethoxysilane reacts with 38.8 g of 90% ethanol, tetrasiloxane is formed as the principal reaction product.

Figure 26 shows the rate of hydrolysis and condensation of ethyltriethoxysilane, and Fig. 27 the effect of the size of the alkyl radical on the rate of hydrolysis of alkyltriethoxysilanes.

Table 49 gives the relation between the number of silicon atoms in the molecules of the principal product of the partial hydrolysis of alkyltriethoxysilane and the molar proportion of water used in hydrolysis; together with the boiling points of the hydrolysis product obtained by me (Bibl. 53).

### Table 49

Relation between the Number of Silicon Atoms in the Polymer Molecule and the Molar Proportion of Water

<table>
<thead>
<tr>
<th></th>
<th>a) Formula of compound hydrolyzed</th>
<th>b) Number of mols of water per mol of product hydrolysed</th>
<th>c) Number of silicon atoms in polymer molecule</th>
<th>d) Boiling point, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_3H_6Si(OC_2H_5)_3$</td>
<td>0.5</td>
<td>2</td>
<td>$R'O[R'Si(OR')_x]R'$</td>
<td>150-155 (10 mm)</td>
</tr>
<tr>
<td></td>
<td>0.65</td>
<td>3</td>
<td></td>
<td>145-150 (0.003 mm)</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>4</td>
<td></td>
<td>195-200 (0.003 mm)</td>
</tr>
<tr>
<td></td>
<td>0.80</td>
<td>5</td>
<td></td>
<td>204-210 (0.003 mm)</td>
</tr>
<tr>
<td></td>
<td>0.85</td>
<td>6</td>
<td></td>
<td>212-220 (0.003 mm)</td>
</tr>
<tr>
<td></td>
<td>0.85</td>
<td>7</td>
<td></td>
<td>224-232 (0.003 mm)</td>
</tr>
<tr>
<td>$(CH_2)_2CHCH_3Si(OC_2H_5)_3$</td>
<td>0.5</td>
<td>2</td>
<td></td>
<td>175-182 (2 mm)</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>4</td>
<td></td>
<td>192-198 (0.001 mm)</td>
</tr>
<tr>
<td></td>
<td>0.85</td>
<td>7</td>
<td></td>
<td>243-249 (0.001 mm)</td>
</tr>
<tr>
<td>$(CH_2)_3CH_2CH_3Si(OC_2H_5)_3$</td>
<td>0.75</td>
<td>4</td>
<td></td>
<td>203-208 (0.002 mm)</td>
</tr>
<tr>
<td></td>
<td>0.80</td>
<td>5</td>
<td></td>
<td>256-260 (0.002 mm)</td>
</tr>
<tr>
<td>$C_4H_9Si(OC_2H_5)_3$</td>
<td>0.65</td>
<td>3</td>
<td></td>
<td>190-204 (0.001 mm)</td>
</tr>
<tr>
<td></td>
<td>0.80</td>
<td>5</td>
<td></td>
<td>272-280 (0.001 mm)</td>
</tr>
</tbody>
</table>

a) Formula of compound hydrolyzed; b) Number of mols of water per mol of product hydrolysed; c) Number of silicon atoms in polymer molecule

$$R'O[R'Si(OR')_x]R'$$; d) Boiling point, °C
It is interesting to note that the length of the siloxane chain of the principal compound formed as a result of the hydrolysis reaction is in complete correspondence with the calculated value (cf. formula on page 352).

Table 50 gives the physical properties of the products of hydrolysis of ethyltriethoxysilane that have been separated.

Table 51 gives the physical properties of the products obtained on the hydrolysis of butyl-, pentyl-, and hexyltriethoxysilanes.

Table 50
Physical Properties of Compounds Separated on Partial Hydrolysis of Ethyltriethoxysilane

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c)</th>
<th>d)</th>
<th>e)</th>
<th>f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethyltetraethoxysiloxane</td>
<td>C₂H₅[Si(CH₃)₂OC₂H₅]₄</td>
<td>150–155°C</td>
<td>1.027</td>
<td>1.4045</td>
<td>56.3</td>
</tr>
<tr>
<td>Triethylpentaethoxysiloxane</td>
<td>C₂H₅[Si(CH₃)₂OC₂H₅]₃</td>
<td>145–150°C</td>
<td>1.062</td>
<td>1.4005</td>
<td>51.8</td>
</tr>
<tr>
<td>Tetraethylhexaethoxysiloxane</td>
<td>C₂H₅[Si(CH₃)₂OC₂H₅]₂</td>
<td>195–200°C</td>
<td>1.082</td>
<td>1.4100</td>
<td>48.0</td>
</tr>
<tr>
<td>Pentaethylheptaoethoxysiloxane</td>
<td>C₂H₅[Si(CH₃)₂OC₂H₅]</td>
<td>264–210°C</td>
<td>1.120</td>
<td>1.4145</td>
<td>47.5</td>
</tr>
<tr>
<td>Hexaethyloctaoethoxysiloxane</td>
<td>C₂H₅[Si(CH₃)₂OC₂H₅]</td>
<td>212–220°C</td>
<td>1.120</td>
<td>1.4140</td>
<td>47.5</td>
</tr>
<tr>
<td>Heptaethylnonaoethoxysiloxane</td>
<td>C₂H₅[Si(CH₃)₂OC₂H₅]</td>
<td>224–232°C</td>
<td>1.120</td>
<td>1.4141</td>
<td>47.5</td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Boiling point, °C; d) Specific gravity, d₂₀; e) Refractive index, n₂₀; f) Content of ethoxy groups, %

The hydrolysis of methyltriethoxysilane has recently been investigated (Bibl.53). On its partial hydrolysis, linear polyethoxymethylsiloxanes of the following general formula C₂H₅O(Si(CH₃)(OC₂H₅))ₓOC₂H₅ have been isolated.

Partial Hydrolysis of Methyltriethoxysilane (Bibl.53). To a solution of 5935 g methyltriethoxysilane in 1525 g of ethanol, a solution of 13.3 g of NaOH in 300 g of water is added over a period of 2 hours. The mixture is allowed to stand over night, and is then heated at boiling point under a reflux condensor. The ethanol formed
during hydrolysis is distilled off, the reaction mixture is heated to 100°C, the reaction product is neutralized by a stream of carbon dioxide gas, and it is then cooled and filtered. The mixture of liquid polymers so obtained (4160 g) is rectified.

Table 52 gives the properties of the compounds so obtained.

The hydrolysis and condensation of unsaturated alkyltriethoxysilanes proceeds according to the same pattern as that of the saturated compounds, but in this case,

<table>
<thead>
<tr>
<th>Physical Properties of Compounds Obtained on Partial Hydrolysis of Alkyltriethoxysilanes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>a)</strong> Name; <strong>b)</strong> Formula; <strong>c)</strong> Boiling point, °C; <strong>d)</strong> Molecular weight; <strong>e)</strong> % Content of Ethoxy groups, %</td>
</tr>
<tr>
<td><strong>Alkyltriethoxysilanes</strong></td>
</tr>
<tr>
<td>Dibutyldiethoxydisiloxane</td>
</tr>
<tr>
<td>Tetrabutylhexethoxytetrasiloxane</td>
</tr>
<tr>
<td>Heptabutylnonethoxyheptasiloxane</td>
</tr>
<tr>
<td>Tetramethylhexethoxytetrasiloxane</td>
</tr>
<tr>
<td>Pentamethylheptasilsiloxane</td>
</tr>
<tr>
<td>Triethylpentamethylpentasiloxane</td>
</tr>
<tr>
<td>Pentamethylheptasilsiloxyne</td>
</tr>
</tbody>
</table>

Together with the hydrolysis and condensation, processes of polymerization also take place, so that the molecular weight of the products of partial hydrolysis is found to be higher. For instance (Bibl.54), when 0.75 mol of water act on 1 mol of allyltriethoxysilane, the molecular weight of the hydrolysis product is 785 instead of the calculated value of 59₄, and when 0.8 mol of water acts, it is 90₉ instead of the calculated 72₄.
Hydrolysis of Alkyltrialkoxy silanes by an Excess of Water

Under the action of an excess of water on individual trifunctional compounds, the products of the reaction of hydrolysis and condensation are no longer linear polyorganosiloxanes, but instead are complex polymers of three-dimensional structure, and we are unable in the general case to calculate the molecular weight of the reaction products mathematically.

Table 52

Physical Properties of the Polymers Obtained as a Result of the Partial Hydrolysis of Methyltriethoxysilane

General Formula of Polymer: C₂H₅O[Si(CH₃)(OC₂H₅)]xOC₂H₅

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c)</th>
<th>d)</th>
<th>e)</th>
<th>f)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>100 (20 mm)</td>
<td>1.24</td>
<td>0.9441</td>
<td>1.3895</td>
<td>70.83</td>
</tr>
<tr>
<td>3</td>
<td>73  (0.5 mm)</td>
<td>1.92</td>
<td>0.9744</td>
<td>1.3934</td>
<td>94.77</td>
</tr>
<tr>
<td>4</td>
<td>95  (0.5 mm)</td>
<td>2.77</td>
<td>0.9835</td>
<td>1.3955</td>
<td>118.56</td>
</tr>
<tr>
<td>5</td>
<td>120 (0.5 mm)</td>
<td>3.48</td>
<td>1.0066</td>
<td>1.3974</td>
<td>142.53</td>
</tr>
</tbody>
</table>

a) Number of silicon atoms, X; b) Boiling point, °C; c) Viscosity, centistokes; d) Specific gravity, d₂⁰; e) Refractive index, n₀⁰; f) Molar refraction

Under the action of excess of water on alkyltrialkoxy silanes at a temperature of 65 - 70°C, there is usually a sharp decrease in the rate of hydrolysis during the first two hours, and equilibrium is practically established. The remaining alkoxy groups are not hydrolyzed for a very long period of time. In this case, the size of the organic radical exerts a rather substantial influence on the number of these residual alkoxy groups. While the number of hydrolyzed alkoxy groups after 1-hour hydrolysis of methyltriethoxysilane is over 90%, this number is only 70% for ethyltriethoxysilane, and during the following 9 hours it does not exceed 75%.

If the hydrolysis reaction is so conducted that the entire amount of water is
introduced at once, at the very beginning of the process, the rate of hydrolysis considerably exceeds the rate of condensation. If the hydrolysis of ethyltriethoxy-silane is almost completed in 1 hour, the refractive index of the mixture and its viscosity still continue to increase for 4 – 6 hours, which is evidence that the process of condensation still continues.

Hydrolysis by Alkali Solutions

The presence of insignificant amounts of alkali during hydrolysis catalyzes the process of cleavage of the alkoxy groups. When concentrated solutions of alkali are used, the following reaction may take place together with the hydrolysis:

\[
\text{Si-OR} + \text{NaOH} \rightarrow \text{Si-ONa} + \text{ROH}
\]

Depending on the reaction conditions, polymers may be formed, containing one atom of sodium per silicon atom, \([\text{RSi(ONa)}]_x\), or disiloxanes, containing two sodium atoms to the silicon atom, \(\text{RSi(ONa)}_2\text{OSi}(\text{ONa})_2\), or monomeric silanolates, \(\text{RSi(ONa)}_3\), containing three sodium atoms to one of silicon. Compounds containing the ONa group are recommended as alkaline catalysts of the rearrangement reaction of cyclic polysiloxanes (Bibl.55).

Hydrolysis of Methyltriethoxysilane in the Presence of Sodium Hydroxide (Bibl. 22). 1. To 7.9 of a saturated aqueous solution of NaOH, a mixture of 17.8 g of methyltriethoxysilane and 19.9 g of methanol is added. When the mixture is allowed to stand, white crystals containing water of crystallization are thrown down. This water of crystallization can be removed by drying the product over phosphorus pentoxide at 140°C.

2. To 17.2 g of methyltriethoxysilane 2.16 g of water and 23.21 g of a saturated aqueous solution of NaOH are added. The ethanol formed is distilled off under a vacuum. Methyl ether is then added to the mixture, separating the crystals of
Compounds containing the ONa group react readily with various alkylchlorosilanes, forming polyorganosiloxanes.

Practical Method of Hydrolysis of Trifunctional Monomers and their Mixtures

In studying the products of hydrolysis and condensation of alkyltrithoxysilanes, I was the first to establish the possibility of preparing high-molecular polyorganosiloxanes possessing a number of technically valuable properties (Bibl.56). The properties of organosilicon resins were studied and their advantages over organic resins were established (Bibl.57).

The hydrolysis of a mixture of substituted esters of functionality higher than two in the presence of acid catalysts, most often of HCl, is of practical importance for the preparation of organosilicon resins. We now present several examples of the practical conduct of this hydrolysis.

1. To a mixture of 7.12 g of methyltrithoxysilane and 1.18 g of trimethyltrithoxysilane, 1.18 g of water is slowly added (in the form of an alcoholic solution containing traces of HCl). The alcohol is distilled off. The product of the hydrolysis (a low-viscosity liquid) is washed and then dried. After air at a temperature of 250°C is blown through it, a solid elastic resin is formed (Bibl.58).

2. On the hydrolysis of butyltrithoxysilane in the presence of 1% of nitric acid, followed by the condensation of the hydrolysis product by blowing air through it for 45 hours at 160°C, a polybutylsiloxane resin of molecular weight 1205 is obtained. The condensation of the product of hydrolysis in the presence of phosphorus pentoxide for 24 hours at 160°C leads to an increase in the molecular weight to 1650 (Bibl.59).

Hydrolysis of mixtures of dimethyldithoxysilane and tetraethoxysilane in the ratios of 2 : 1 and 3 : 1, under the same conditions, yields a resinous polymer (Bibl.60).
One of the most important methods of preparing resinous polysiloxanes is the hydrolysis of the reaction mixtures obtained by the alkylation of tetraethoxysilane by organomagnesium compounds. By regulating the degree of alkylation, resins with various physical and chemical characteristics may be obtained. For instance, on the hydrolysis of a mixture of ethylethoxysilanes, obtained by the reaction between tetraethoxysilane, magnesium, and ethyl bromide, in the presence of sulfuric acid, followed by washing, drying, and condensation, a polyethoxysiloxane resin is formed (Bibl.45).

**Alcoholysis and Reesterification**

Under the action of alcohols on substituted esters, the reaction of alcoholysis takes place. This process has all the features indicated in our discussion of the alcoholysis of esters of orthosilicic acid on page 249. The distinctive feature of the reaction in this case is merely the lower activity of the substituted ester as compared with the tetraalkoxysilanes; thus, for example, the reaction between ethyl-triethoxysilane and normal propyl alcohol by the formula

\[
\text{SiH}_{3} (\text{OCH}_{3})_3 + 3\text{C}_2\text{H}_5\text{OH} \rightarrow \text{SiH}_{3} (\text{OCH}_{3})_2\text{CH}_3 + 3\text{H}_2\text{O}
\]

proceeds on heating the reaction mixture to the boiling point and distilling off the ethanol formed over a period of 95 hours (Bibl.33).

If the reaction of alcoholysis is conducted by reacting the substituted ester with polyethylene glycol, then the reaction products are water soluble (Bibl.61).

The alcoholysis of compounds of the type \(R\text{Si}(\text{OC}_2\text{H}_5)_3\), where \(R\) is an aliphatic radical containing from 12 to 24 carbon atoms, proceeds at a temperature of the order of 200 - 300°C. The reaction product are surface-active and may be used as emulsifiers or in order to render various materials water-repellant.

A weak acid, like an alcohol, may enter into a reaction with a substituted ester; for example, boric acid in the presence of an acid catalyst, forms the corresponding silylborate:
Preparation of Tri-(trimethylsilyl)-Borate (Bibl.62). A mixture of 35.5 g of trimethylethoxysilane, 6.2 g of boric acid, and 10 mg of toluenesulfonic acid is heated at boiling point for 5 hours. The reaction product contains tri-(trimethylsilyl)-borate, boiling point 90°C, refractive index $n_D^{20^\circ} = 1.3839$.

When two substituted esters react with each other, metathesis of the alkoxy groups takes place (Bibl.63):

$$3(\text{CH}_3\text{SiO})_2\text{CH}_2\text{OH} + \text{H}_3\text{BO}_3 \rightarrow \text{B}[\text{OSi}(\text{CH}_3)_3]_2 + 3\text{CH}_3\text{OH}$$

Replacement of an Alkoxy Group by a Halogen Atom

This reaction is similar to the corresponding reaction of the esters of orthosilicic acid, but leads instead to the formation of alkyl-(aryl)-halosilanes:

$$(\text{C}_3\text{H}_7)_3\text{SiOC}_2\text{H}_4 + \text{CH}_3\text{COCl} \rightarrow (\text{C}_3\text{H}_7)_3\text{SiCl} + \text{CH}_3\text{COOC}_2\text{H}_4$$

Preparation of Tripropylchlorosilane (Bibl.18). A mixture of 7 g of tripropylethoxysilane and 16 ml of acetyl chloride is heated, and at the same time the ethyl acetate is distilled off. In this case 5.5 g (85%) of tripropylchlorosilane is formed.

A similar reaction takes place when substituted esters react with benzoyl chloride when heated for many hours at 200°C in a sealed tube (Bibl.64). In the presence of quinoline phosphate, this reaction proceeds very well even in an open vessel communicating with the atmosphere. This method is recommended for the preparation, for instance, of pure dimethyldichlorosilane from dimethyldibutoxysilane (yield 80%), and also for preparing methylchlorosilanes from methylchloroethoxysilanes.

The replacement of alkoxy groups by halogen atoms likewise takes place under the action of phosphorus trichloride; for instance, trimethylethoxysilane reacts at 70°C:
3(CH₃)₃SiOC₂H₆ + PCl₅ → 3(CH₃)₃SiCl + P(OC₂H₅)₃

At high temperatures, the reaction of phosphorus chlorides with substituted esters is more complicated, an alkyl chloride being liberated and polysiloxane formed (Bibl.64).

The replacement of an alkoxy group by fluorine is considerably easier than by chlorine. The reaction proceeds easily under the action of hydrofluoric acid (Bibl.65):

C₆H₅Si(OC₂H₅)₃ + 3HF → C₆H₅SiF₃ + 3C₂H₅OH

Cleavage of Alkoxy Groups and Formation of Organosiloxanes

The reactions recalling the processes of hydrolysis, which occur under the action, mainly, of acids on the substituted esters, are of great practical importance. HI quantitatively converts substituted esters into polyorganosiloxanes (Bibl.66):

xRSi(OCH₃)₃ + 3xHJ → (RSiO)ₓ + 3xC₂H₅J + 1.5xH₂

Dilute sulfuric acid has a similar action:

2(C₂H₅)₃SiOC₂H₆ + H₂SO₄ → (C₂H₅)₃SiOSi(C₂H₅)₃ + 2C₂H₅OSO₃H

and also the lower organic acids (Bibl.66):

R₂Si(OR')₄₋ₓ + (4₋ₓ)RCOOH → [(R₂SiO)ₓ] + (4₋ₓ)RCOOR' + 4₋ₓ/2H₂O

Preparation of Polymethylsiloxane. A mixture of 3₄.5 g of formic acid, 5₈.5 g of amyltriethoxysilane, and 0.₅—1 g of p-toluenesulfonic acid, is heated to the boiling point, and the ethyl formate (5₅ g) is simultaneously distilled off, thus forming polymethylsiloxane.

These reactions may serve for the quantitative cleavage of the alkoxy groups and accomplishment of hydrolytic processes.

Of interest is the catalytic cleavage of alkoxy groups in substituted halo-
esters on heating in the presence of ferric chloride, and also the cleavage of alkoxy groups on heating a mixture of substituted esters and alkylchlorosilanes in the presence of ferric chloride. The process, schematically represented by the equation:

\[
\text{Si-OR + Cl-Si} \rightarrow \text{Si-O-Si} + \text{RCI}
\]

leads to the formation of various polyalkysiloxanes (Bibl.67).

The amount of ferric chloride used ranges from 0.03% to 1%. The most varied products may enter into this reaction (dimethylalkoxychlorosilanes, the product of partial esterification of a mixture of phenyl- and methyltrichlorosilanes and phenylmethylidichlorosilane, a mixture of methyltriethoxysilane, phenyltrichlorosilane, and dimethylidichlorosilane, etc.). With a proper selection of the proportion between these components, various polyalkyl-(aryl)-siloxanes containing neither chlorine atoms nor alkoxy groups may be obtained.

The reaction between the substituted esters and acetic anhydride (Bibl.67) proceeds similarly to the reaction of esters of orthosilicic acid:

\[
\text{C}_3\text{H}_5\text{Si(OR)}_3 + 3\text{(CH}_3\text{CO})_2\text{O} \rightarrow \text{C}_3\text{H}_5\text{Si(OOC}_3\text{H}_5) + 3\text{CH}_3\text{COOR}
\]

If \( R = \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{or C}_4\text{H}_9 \), the reaction proceeds at the boiling point of the mixture, in almost quantitative yield. The reaction product may dissociate in the acetic anhydride medium, so that a side reaction may occur, leading to the formation of polyorganosiloxanes:

\[
\begin{align*}
\text{C}_3\text{H}_5\text{Si(OR)}_3 + \text{(CH}_3\text{CO})_2\text{O} & \rightarrow \text{C}_3\text{H}_5\text{Si(OR)}_2(\text{OCOCH}_3) + \text{CH}_3\text{COOR} \\
\text{C}_3\text{H}_5\text{Si(OR)}_2(\text{OCOCH}_3) & \rightarrow \text{C}_3\text{H}_5\text{Si(OR)}_2 + \text{CH}_3\text{CO}- \\
\text{C}_3\text{H}_5\text{Si(OR)}_2(\text{OCOCH}_3) & \rightarrow \text{C}_3\text{H}_5\text{Si(OR)}_2(\text{OCOCH}_3) + \text{CH}_3\text{CO}- \\
\text{RO} & \text{C}_3\text{H}_5\text{Si(OR)}_2(\text{OCOCH}_3) + \text{CH}_3\text{Si(OR)}_2 + \text{H}_3\text{C}-\text{Si}(\text{OR})_2 + \text{etc.}
\end{align*}
\]

Cleavage of Organic Radicals

Under the action of an alkali, and, in certain cases, of water, on substituted
esters whose molecules contain chlorinated aliphatic radicals or radicals with multiple bonds, cleavage of these groups takes place:

\[ \text{Si} \quad \text{R} \quad \text{HOH} \quad \rightarrow \quad \text{Si} \quad \text{OH} \quad + \quad \text{RH} \]

Cleavage of groups with a triple bond at the α-carbon atom is particularly easy. Vol'nov and Reutt (Bibl.10) found that when phenylacetylenetriethoxysilane is treated with boiling water, a certain amount of phenylacetylene is formed, as well as a mixture of benzene-insoluble and benzene-soluble polymeric products of hydrolysis. Obviously, both reactions of hydrolysis, leading to the formation of a polysiloxane soluble in benzene

\[ \text{C}_9\text{H}_5\text{C} \quad \quad \text{(SiO}_2\text{H})_x \quad \rightarrow \quad (\text{C}_9\text{H}_5\text{C} \quad \quad \text{SiO}_1.5)_x \]

and a cleavage reaction, leading to the formation of silica gel:

\[ (\text{C}_9\text{H}_5\text{C} \quad \quad \text{SiO}_1.5)_x \quad \rightarrow \quad (\text{SiO}_2)_x \]

must take place.

**Formation of Polymeric Substituted Esters**

When glycols react with alkylchlorosilanes, the reaction product is a polymer with the structural unit:

\[ \text{R} \quad \quad \text{OR} \quad \quad \text{Si} \quad \quad \text{OR'} \quad \quad \text{O} \]

and the silicon atom may be bound by its fourth valence either with the organic radical R, or with the glycol residue OR'O. These compounds may be prepared by esterification of organochlorosilanes or by alcoholysis of substituted esters. The only difference is that, instead of a monatomic alcohol, diatomic glycols (Bibl.68) or phenols are used in the reaction. The presence of a second reactive group in the molecule of the glycol (or phenol) leads to the formation of a polymer which is usu-
ally of cyclic structure

\[ R_2SiCl + xHOR'OH \rightarrow (R_2SiOR')_x + 2xHCl \]

or

\[ R_2Si(OC_2H_5)_2 + xHOR'OH \rightarrow (R_2SiOR')_x + 2xC_2H_5OH \]

If a trifunctional compound is introduced into the reaction instead of a bifunctional compound, a polymer of cross-linked structure is obtained.

When ethylene glycol is heated with dimethyldichlorosilane at 55°C in the presence of p-toluenesulfonic acid, a polymer is formed, which is a liquid with the molecular weight 1164 (x = 10):

\[ [(CH_2)_3Si(OCH_2CH_2O)_x ] \]

When this polymer is heated to higher temperatures, its molecular weight diminishes. Destructive distillation of the polymer yields crystals of the same composition and a molecular weight of 243(x = 2), which on standing are again converted into a liquid.

According to patent data (Bibl.68), the esterification of dialkyldichlorosilanes may be conducted by the action of diphenylpropane, deca- or hexamethylene glycol, 4,4-dioxydiphenyl, etc. The reaction is catalyzed by sodium in amounts ranging from 0.002% to 1%. The reaction of diethyldiphenoxysilane with diphenylolpropane leads to the formation of a viscous polymer which is suitable for the production of glues and adhesive materials.
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CHAPTER VI

ALKYL-(ARYL)-HALOSILANES AND HALOALKYL-(HALOARYL)-HALOSILANES

Alkyl-(Aryl)-Halosilanes

The alkyl-(aryl)-halosilanes constitute an extensive group of monomeric organosilicon compounds.

The alkyl-(aryl)-chlorosilanes are the compounds of this class that are of the greatest practical importance and are most available.

The group of alkyl-(aryl)-chlorosilanes includes compounds of the types:

\[
\begin{align*}
& \text{RSiH}_2\text{Cl}, \quad \text{R}_2\text{SiHCl}, \quad \text{RSiCl}_2 \\
& \text{I} \quad \text{II} \quad \text{III} \\
& \text{R}_3\text{SiCl} \quad \text{R}_2\text{SiCl}_2 \\
& \text{RSiCl}_3
\end{align*}
\]

Compounds of the first group (1) have been little studied, and their number of synthesized compounds is insignificant. The compounds of the second group (2), which are more important, have been synthesized in larger number, and many of them have also been studied in detail.

The high chemical activity of the halogen in alkyl- and aryl-chlorosilanes permits their wide use for various reactions with organic compounds. Their reaction with water is particularly interesting. Under the action of water, alkyl- and aryl-halosilanes easily exchange the halogen atom for a hydroxyl group; thus forming alkyl- and arylsilanols, from which high-polymeric compounds (polyorganosiloxanes),
possessing very valuable technological properties, are prepared.

**Preparation of Alkyl-(Aryl)-Chlorosilanes**

The alkyl-(aryl)-chlorosilanes are the most important class of monomeric organosilicon compounds. They are one of the principal intermediates for the preparation of organosilicon polymers, and may be manufactured in large amounts by simple and economical methods.

In most chemical reactions, the organic radicals attached to the silicon atom remains unchanged, but the halogens do participate in the reaction. For this reason the alkyl-(aryl)-chlorosilanes are divided, according to their functionality, into the following groups:

I. Trifunctional - alkyl-(aryl)-trichlorosilanes.

II. Bifunctional - dialkyl-(diaryl)-dichlorosilanes.

III. Monofunctional - trialkyl-(triaryl)-chlorosilanes.

Alkyl-(aryl)-chlorosilanes are prepared by two principal methods of synthesis:

1. by substituting organic radicals for chlorine atoms in SiCl or in organochlorosilanes, by the aid of organomagnesium or other organometallic compounds;

2. by the direct reaction of an alkyl halide with silicon in the presence of a catalyst (direct synthesis).

Other methods of synthesis have not yet acquired practical importance.

**Preparation of Alkyl-(Aryl)-Chlorosilanes by the Aid of Organomagnesium Compounds**

In evaluating the method of preparing alkylchlorosilanes by the aid of organomagnesium compounds, its universality and flexibility should first of all be pointed out. In reactions with organomagnesium compounds, alkyl-(aryl)-chlorosilanes combining in themselves various different organic radicals may be prepared. In this respect this method excels all others, except for that of synthesis with organolithium compounds, which, however, cannot be widely used owing to the high cost of
Under laboratory conditions, synthesis by the aid of organomagnesium compounds is the most valuable and universal method for preparing both alkyl-(aryl)-chlorosilanes and a considerable number of other organosilicon compounds.

The inconvenience involved is the unavoidability of using a solvent or diluent, sometimes in substantial amounts, and also the necessity of separating the precipitate of magnesium salts. All this makes a large number of stages necessary, makes the process prolonged and leads to the low productivity of the apparatus. This fact considerably reduces the value of this method for preparing organosilicon compounds on an industrial scale. Direct synthesis, which has certain other disadvantages, does not, however, have the disadvantages inherent in the method of substitution through organomagnesium compounds, and therefore a combination of these two methods makes it possible the rational preparation of the overwhelming majority of the alkyl-(aryl)-chlorosilanes.

The organomagnesium compounds however, which were discovered in the first years of the present century, soon found use for the synthesis of the alkyl-(aryl)-chlorosilanes in the presence of ethyl ether.

The reaction with SiCl$_4$ proceeds according to the mechanism

$$
\begin{align*}
\text{SiCl}_4 + \text{RMgX} &\rightarrow \text{RSiCl}_3 + \text{MgX}_2 \\
\text{RSiX}_3 + \text{RMgX} &\rightarrow \text{R}_2\text{SiX}_2 + \text{MgX}_2 \\
\text{R}_2\text{SiX}_2 + \text{RMgX} &\rightarrow \text{R}_3\text{SiX} + \text{MgX}_2 \\
\text{R}_3\text{SiX} + \text{RMgX} &\rightarrow \text{R}_4\text{Si} + \text{MgXX}
\end{align*}
$$

When SiCl$_4$ is mixed with a solution or suspension of alkyl-(aryl)-magnesium halide, a mixture of alkyl-(aryl)-chlorosilanes of all degrees of substitution is usually formed.

The ratio between the reaction products depends primarily on the ratio between the starting reagents. By selecting the proper proportions, the process may at will be directed toward the production primarily of the alkyltrichlorosilane, the dialkyl dichlorosilane, or the trialkylchlorosilane.
Another condition affecting the ratio between the reaction product is the relative reactivity of the tetrahalosilane and the products of varying degrees of alkylation.

If both these conditions are known, then the ratio between the different reaction products may be calculated (for the ideal case, when the velocity of introduction of the organomagnesium compound is infinitesimal, and ideal mixing is assured).

Let:

\[ x = \text{ratio of the number of mols of organomagnesium compound to the number of mols of } \text{SiCl}_4; \]

\[ y = \text{ratio of number of mols of products of various degrees of substitution, } R_n\text{SiCl}_{4-n}, \text{ formed, to the number of mols of } \text{SiCl}_4 \text{ taken into the reaction;} \]

\[ 1:x:R:y = \text{ratio between reaction rates between the organomagnesium compound and the } \text{SiCl}_4, \text{ the alkyltrichlorosilane, the dialkyldichlorosilane, and the trialkylchlorosilane respectively;} \]

\[ N = \text{number of mols of } \text{SiCl}_4. \]

The process reflecting the above reactions between \( \text{SiCl}_4 \) and \( R_n\text{M}_gX \) may in the general case be mathematically described by the following system of differential equations (Bibl.1):

\[
\begin{align*}
\frac{dy_0}{dx} &= -\gamma y_0dx \\
\frac{dy_1}{dx} &= \gamma (y_0 - \alpha y_1)dx \\
\frac{dy_2}{dx} &= \phi (y_2 - \beta y_2)dx \\
\frac{dy_3}{dx} &= \gamma (y_3 - \gamma y_3)dx \\
\frac{dy_4}{dx} &= \gamma y_4dx
\end{align*}
\]

where

\[ \gamma^{-1} = N(y_0 + \alpha y_1 + \beta y_2 + \gamma y_3) \]

The solution of these equations allows us to elucidate the relation between the relative amount of organomagnesium compounds \( x \), the ratio between the reaction rates (the reactivity) and the relative quantity \( y_n \) of the compounds of various degrees of substitution, \( R_n\text{SiCl}_{4-n} \) in the reaction products.
These equations allow us theoretically to calculate the ratio of the alkyl-(aryl)-chlorosilanes in the mixture formed under the action of the organomagnesium compound on SiCl₄ for definite ratios between the reaction rates of the chlorosilanes.

By studying the ratios between the starting reagents and the reaction products, it is possible to draw a conclusion as to the ratio between the reaction rates of the various chlorosilanes.

There is today unfortunately not a sufficient amount of experimental material available that would allow us to elucidate this question completely. It can only be stated that, in general, the relative reactivity of the chlorosilanes depends on the type of radicals attached to the silicon atom, as well as on their number and on the symmetry of the molecular structure. The symmetrical dialky-(diaryl)-dichlorosilanes react at a considerably lower velocity than the asymmetric monalkyltrichlorosilanes, that is, the velocity of reaction is usually considerably smaller than the value of \( \alpha \) which sometimes exceeds 1. If the molecular symmetry is not of substantial importance, then the hypothesis that the respective reactivities are in the following ratio

\[ 1 : \frac{3}{4} : \frac{1}{2} : \frac{1}{4} \]

is the most probable. In this case, the above equations will take
the following form:

\[
\begin{align*}
y_1 &= 4y_0 \left( \frac{y_0}{y_0} - 1 \right) \\
y_2 &= 6y_0 \left( \frac{y_0}{y_0} - 1 \right)^2 \\
n_0 &= 4y_0 \left( \frac{y_0}{y_0} - 1 \right)^3
\end{align*}
\]

Then

\[
x = 4 \left( 1 - y_0 \right)
\]

In the case where the molecular symmetry has a substantial influence on the course of the product, the value of \(\alpha\) must be taken higher. If the ratio of the substances in the reaction mixture

\[
1 : a : b : 1 : 2 : \frac{1}{3} : \frac{2}{3}
\]

then

\[
\begin{align*}
y_1 &= y_0(1 - n_0) \\
y_2 &= \frac{4}{3}(2y_0^2 - y_0^3 - 3y_0) \\
n_0 &= 27y_0^3 + 6y_0 - 27y_0^3
\end{align*}
\]

In that case

\[
x = 1 - \frac{40}{3}y_0^3 + 5y_0 - \frac{12}{3}y_0 + \frac{27}{2}y_0
\]

For each given ratio between the reactivity, a curve of a relationship between the yield of any of the alkyl-(aryl)-chlorosilanes \(y_n\) and the ratio between the number of mols of organomagnesium compounds and that of \(\text{SiCl}_4\) can be constructed. A comparison of the experimental data on the composition of the mixtures with the course of the curves for various reactivity ratios may give an idea of the relative reactivity of a number of alkyl-chlorosilanes with respect to a given organomagnesium compound; when the reactivity is known, however, the composition of the reaction products can be mathematically calculated (under ideal conditions) for any desired ratio between the organomagnesium compound and the \(\text{SiCl}_4\).

As already stated, we lack today, for the solution of this problem, exhaustive
experimental data which would make it possible precisely to establish the reactivity ratio, even for compounds with simple organic radicals. It can only be said roughly, for purposes of orientation, that, for example, for the characteristic of the reaction between SiCl_{4} and phenylmagnesium bromide in a medium of ethyl ether, the curves of the relation between \( y_n \) and \( x \), calculated by the ratio \( \frac{1}{2} : \frac{2}{3} \), come closest. This is evidence that in the reaction with phenylmagnesium bromide, the molecular symmetry of chlorosilane substantially influences the reactivity (the asymmetric phenyltrichlorosilane reacts twice as fast as SiCl_{4}, and four times as fast as diphenyldichlorosilane). The difficulties of preparing phenyltrichlorosilane by means of organomagnesium compounds are related to this fact. On the other hand, there are grounds for considering that ethyltrichlorosilane has a lower reactivity with respect to ethylmagnesium bromide than SiCl_{4} has, and therefore it can be easily prepared in high yield.

In practice, the amount of organomagnesium compound is usually taken in 25% excess for the replacement of a chlorine atom in SiCl_{4} by an organic radical. For example, for the synthesis of a dialkyl-(diaryl)-dichlorosilane, 2.5 mols of the corresponding organomagnesium compounds is taken for each mol of SiCl_{4}. If the object of the synthesis is to replace one atom of chlorine in SiCl_{4}, and excess of SiCl_{4} is usually used, and after the completion of the process this excess is easily separated.

The synthesis of an organomagnesium compound in the presence of ethyl ether, which has given a good account of itself in laboratory practice, is inconvenient under industrial conditions, although, according to the literature, it is used in the United States for the synthesis of organosilicon polymers. The method of preparing organomagnesium compounds proposed by me (Bibl.2) enables us to synthesize the alkyl-(aryl)-chlorosilanes without using ethyl ether as a solvent.

This process may be run either in two stages, with the preliminary preparation of the organomagnesium compounds, by the reactions:

\[
\begin{align*}
\text{Mg} & \rightarrow \text{RMgX} \\
\text{SiCl}_4 & + \text{RMgX} \rightarrow \text{RSiCl}_3 + \text{MgCl}_2 \text{ etc.}
\end{align*}
\]
or in a single stage, by the reaction between magnesium and a mixture of $\text{SiCl}_4$, alkyl halide, solvent, and catalytic quantities of tetraethoxysilane.

Preparation of Ethyltrichlorosilane and Diethyldichlorosilane without use of Ether (Bibl.3). In a round bottom flask, provided with a stirrer with mercury seal, a dropping funnel, a thermometer lowered to the bottom of the flask, and a reflux condenser with a calcium chloride tube, 12 g of freshly prepared dry magnesium shavings, less than 0.1 mm thick, are placed with a few drops of tetraethoxysilane. From the dropping funnel 1 to 2 ml of ethyl bromide are introduced into the flask, after which the temperature in the flask usually rises rapidly to 70-80°C. The stirrer is now started. The reaction mixture is slightly cooled on a water bath, and the ethyl bromide is added slowly (dropwise). The first portion of ethyl bromide (40 g), is added under constant cooling of the mixture on a water bath. The process in this stage is usually strongly exothermic; the flask is filled with a white mist; when the cooling bath is removed, the temperature of the mass sharply rises. The remaining ethyl bromide, 22 g, is added together with a solvent, thoroughly dried benzene or toluene (70 g). If the temperature of the reaction mass begins to fall, the mass is slightly heated on a water bath (in such a way as to hold the temperature of the mixture at about 45°C during the course of the addition of ethyl bromide). When the addition of the ethyl bromide is finished, the mixture is heated to the boiling point, until the dissolution of the magnesium is completed (3-4 hours); the reaction mixture is then cooled to 10-15°C, and then, with stirring, a solution of 85 g of $\text{SiCl}_4$ and 100 g of solvent is rapidly poured into it. The mixture is stirred at room temperature for half an hour, and is then gradually heated to the boiling point and held at this temperature until no more organomagnesium compound remains in a sample of the reaction mass.

A qualitative analysis for the presence of the organomagnesium compound may be made as follows. A sample 1-0.5 g of the reaction mixture is mixed with half the volume of a 1% solution of Michler's ketone in benzene. The mixture is then treated.
with a few drops of water and is vigorously shaken, after which 2-3 drops of a 1% solution of iodine in acetic acid is added. The appearance of a green or blue color indicates the presence of an organomagnesium compound in the original reaction mixture. If the sample does not change color, the synthesis is considered to have been completed. The mixture is now transferred to a Wurtz flask, or to a metal retort, for distillation of the liquid from the precipitate of magnesium chlorobromide. When the distillation under atmospheric pressure has been completed, the vacuum pump is turned on, and the distillation is continued until no more condensate arrives in the receiver. The distilled liquid is rectified in a column with 20-30 theoretical plates, the ethyltrichlorosilane is collected at 98-100°C, and the diethyldichlorosilane in the range 128-130°C. The yield of ethyltrichlorosilane is 65 g, or 80% of theoretical.

If the object is to get mostly diethyldichlorosilane, the technique of the process remains the same, but the ratio of the reagents is modified (to 1 mol of SiCl\textsubscript{4}, 2-2.5 mols of magnesium and 2.4-2.8 mols of ethyl bromide are taken instead). The yield of diethyldichlorosilane in this case is 70% theoretical.

The conduct of the synthesis in a single stage makes it possible in most cases easily to regulate the process and obtain better yields. In this case, it is more convenient to conduct the synthesis by pouring a mixture of SiCl\textsubscript{4}, ethyl bromide, solvent, and catalytic amounts of tetraethoxysilane (in the ratios indicated above) onto the magnesium shavings, moistened with a few drops of tetraethoxysilane. To accelerate the process, it is advisable to introduce ethyl ether into the mixture in an amount not exceeding 1%. The addition of the mixture takes 3-4 hours at a temperature of 45°C, after which it is gradually heated to the boiling point. The process is followed, and the mixture is separated, according to the above described technique.

The use of ether in the process does not increase the yield of the reaction product.
Preparation of a Mixture of Ethylchlorosilanes in an Ether Medium in Two Stages (Bibl.4). In a 5-liter flask, provided with a stirrer with mercury seal, a reflux condenser with a calcium chloride tube, a thermometer, and a dropping funnel, 178 g of magnesium shavings and 1250 ml of absolute ether, containing traces of iodine are placed. Into the flask 10 ml of ether bromide is introduced, and then 500 ml of ethyl bromide and 15 ml of ethyl ether are slowly and uniformly poured in. The dissolution of the magnesium is completed in 3 to 4 hours, thus forming a 2.5-mol solution of ethylmagnesium bromide. A solution of ethylmagnesium bromide so obtained so prepared (3 liters) is added uniformly over a period of 3 hours to a solution of 345 ml of SiCl₄ in 625 ml of ethyl ether. When the addition of the solution has been completed, the mixture is heated half an hour at the boiling point, after which it is cooled, the liquid is decanted, and the residue is extracted with ether. The excess, after distilling off the ether, is fractionated, yielding 25-30 ml of a fraction boiling at 95-105°C (impure ethyltrichlorosilane), 200 ml of a fraction boiling at 125-135°C (impure diethyldichlorosilane), and 25-35 ml of a fraction boiling above 140°C, which contains triethylchlorosilane. Thus the yield of the mixture of unpurified ethylchlorosilanes does not exceed 60% of theoretical (based on SiCl₄).

Ethyltrichlorosilane (Bibl.5) may be prepared by a similar method, using a considerable excess of SiCl₄ (5 mols of SiCl₄ per mol of C₂H₅MgBr) (Bibl.5). The yields of ethyltrichlorosilane is 48% (based on the starting magnesium).

The preparation of methylchlorosilanes (Bibl.6) by means of organomagnesium compounds involves two basic difficulties. First, the starting alkyl halides, methyl chloride and methyl bromide, are gases under ordinary conditions; second, the organomagnesium compound reacts with excessive violence with the SiCl₄, thus making it difficult to regulate the process, and which may also lead to the formation of considerable amounts of tetramethylsilane instead of the methylchlorosilanes desired.

In comparing the reactivity of methylmagnesium bromide, for example, with that of ethylmagnesium bromide, we may point to the fact that on the action of a mixture
of methyl- and ethylmagnesium bromides on triethylchlorosilane, only triethylmethylsilane is formed.

The high reactivity of methylmagnesium halides forces the conduct of the synthesis of methylchlorosilanes under particularly mild conditions.

**Preparation of a Mixture of Methylichlorosilanes in an Ether Medium.** A mixture of 212.5 g of SiCl₄ and 350 ml of dibutyl ether is placed in a 5-liter flask provided with a stirrer and a reflux condenser. The flask and the condenser are cooled to -78.5°C. To the mixture, with vigorous stirring, 3.3 liters of a molar solution of methylmagnesium chloride (or bromide) in ether is added over a period of 2.5 hours. Then, under stirring, the mixture is gradually warmed to room temperature and allowed to stand. The product is separated from the residue of magnesium chloride by decantation and extraction with ether. The ether is distilled off, and the residue is rectified in a column of 60-70 theoretical plates. The methyltrichlorosilane is collected in the range 66-67°C, and the dimethyldichlorosilane in the range 69-70°C.

The mixture of methylchlorosilanes so obtained consists mainly of dimethyldichlorosilane is desired, a solution of 476 £ of SiCl₄ in 750 ml of dibutyl ether is acted on by 2.9 liters of a 1.8 molar solution of methylmagnesium chloride in ethyl ether. It is difficult to prepare pure trimethylchlorosilane in this way, since it forms an azeotrope with SiCl₄. It is far more convenient to prepare trimethylchlorosilane from pure dimethyldichlorosilane or methyltrichlorosilane, or from mixtures of these substances, the intermediate fractions collected between 67 and 69.5°C on the rectification of the methylchlorosilanes.

**Preparation of Trimethylchlorosilane.** In one liter of ether is dissolved 429.5 g of a mixture obtained on the rectification of the methylchlorosilanes at 67-69.5°C, containing 2.75 mols of dimethyldichlorosilane and 0.5 mol of methyltrichlorosilane. The solution is placed in a flask cooled by a mixture of solid carbon dioxide and acetone. Under stirring, 500 ml of a 4.1 mol solution of methylmagnesiumchloride is gradually added, and the mixture is gradually warmed to room
temperature. The liquid is then decanted, the ether is distilled off, and the trimethylchlorosilane is separated by rectification in a column with 40 theoretical plates. The trimethylchlorosilane so prepared has a boiling point of 57.5°C. The yield is 38.7 g (0.35 mol).

The synthesis of the methylchlorosilanes from organomagnesium compounds and SiCl₄ has not had practical importance, owing to the difficulties described above, on the one hand, and also, on the other hand, owing to the simplicity and accessibility of the direct synthesis of the methylchlorosilanes from silicon and methyl chloride.

The reaction with methylmagnesium chloride, however, still maintains its importance wherever it is necessary to insert a methyl radical into a molecule of various alkyl or arylchlorosilanes.

Many alkylchlorosilanes may be prepared in a similar way, either by the reaction of an alkylmagnesium chloride with SiCl₄ in an ether solution, or without using ether, that is, by the action of a mixture of an alkyl halide, SiCl₄, a solvent (benzene, toluene, xylene) and catalytic quantities of tetraethoxysilane, on magnesium. For the synthesis of the alkyltrichlorosilanes, it is advisable to use an excess of SiCl₄ (1.5-2 mols of SiCl₄ to each mol of alkylmagnesium chloride). This excess of SiCl₄ can easily be separated from many alkyl- and arylchlorosilanes (except methylchlorosilanes) owing to their relatively low boiling points. The dialkylchlorosilanes are prepared by the action of 2.25 mols of an alkylmagnesium chloride (or of the corresponding amounts of magnesium and alkyl chloride) on 1 mol of SiCl₄.

Trialkylchlorosilanes are formed either on the action of an excess of alkylmagnesium halide (4 mols) on 1 mol of SiCl₄, or by alkylation of a dialkylchlorosilane.

With increasing length of the organic radical, the velocity of the reaction between the organomagnesium compound and SiCl₄ decreases, and a more prolonged heating of the mixture is necessary to complete it. We present as an example a method of
synthesizing dodecyltrichlorosilane.

Preparation of Dodecyltrichlorosilane in an Ethereal Medium (Bibl.7). Into a flask containing 12.5 g of magnesium shavings and 35 g of ethyl ether, a solution of 95 g of dodecyl chloride in 68 g of ether is gradually poured. The dissolution of the magnesium is completed when the mixture is heated on a water bath for an hour, after which the solution so prepared is slowly added, with stirring, to a mixture of 140 g of SiCl$_4$ in 150 g of dry benzene. The reaction is completed on boiling the mixture 3-5 hours. The dodecyltrichlorosilane is separated from the reaction mixture by decantation, extraction, and rectification. It boils at 162-171°C (18 mm). The yield of the product is 67% of theoretical. Tetradecyltrichlorosilane and octadecyltrichlorosilane can be prepared similarly, using corresponding proportions of the reagents.

Another factor which has a considerably stronger influence on the rate of reaction of an alkylmagnesium chloride with SiCl$_4$ is steric hindrance. As a rule, in single-stage alkylation, only a single branched radical can be introduced into the SiCl$_4$ molecule. To add a second such radical, the alkyltrichlorosilanes so obtained must be acted on by an excess of the organomagnesium compound. It has not been possible, however, to insert a third organic radical into the compound by the aid of organomagnesium compounds. Such reactions are accomplished by means of organolithium compounds.

The reaction between phenylmagnesium bromide and SiCl$_4$ in an ether solution proceeds readily. In this case two chlorine atoms in the SiCl$_4$ are replaced. Phenyltrichlorosilane has not been prepared in high yield, obviously owing to the fact that the asymmetric phenyltrichlorosilane reacts with phenylmagnesium bromide at a higher velocity than the SiCl$_4$ does. Even when an excess of SiCl$_4$ is used, the yields of phenyltrichlorosilanes does not exceed 30% of theoretical. When phenylmagnesium bromide acts on SiCl$_4$ (2.25 mols to 1 mol) the following are obtained: 14% of phenyltrichlorosilane, 64% of diphenyldichlorosilane, and 5% of triphenylchlorosilane.
Koton (Bibl.9) has prepared phenylchlorosilanes by the action of ether solution of phenylmagnesium bromide on SiCl$_4$, but he did not separate the product from the reaction mixture, hydrolyzing them instead to prepare polyphenylsiloxane resin.

Preparation of Phenylchlorosilanes in an Ether Medium (Bibl.9). In a flask provided with stirrer, reflux condenser, and dropping funnel, 15 g of magnesium shavings by iodine are placed, and a mixture of 100 g of bromobenzene and 100 ml of ether is then added dropwise. When the addition of the mixture has been completed, the reaction mass is heated on a water bath until the magnesium is completely dissolved.

The reaction product is slowly poured, with stirring and cooling, into a mixture of 100 g of SiCl$_4$ and 100 ml of ether. The reaction mass is heated on the water bath and is held at boiling point for 2 to 3 hours. The precipitate of magnesium chlorobromide is removed by filtration, the ether is distilled off, and the residue, a mixture of phenylchlorosilanes with an admixture of diphenyl, is hydrolyzed. After extraction, drying, and evaporation, 70 g of polyphenylsiloxane resin, containing 38% of SiO$_2$, is separated. The yield of the product is 32% of theoretical (based on SiCl$_4$). It is not possible to establish precisely from the literature the quantity and nature on the reaction products, but the low SiO$_2$ content in the reaction product, in spite of the obvious presence of the hydrolysis products of SiCl$_4$ in it, is evidence that not only phenyltrichlorosilane, as the author considers, was formed during the synthesis, but also diphenylchlorodichlorosilane.

In a study of the reaction of phenylmagnesium bromide with SiCl$_4$ in ether solution (Bibl.8), it was found that the reaction product contained mixed halo-esters, whose formation is due to the reaction between ether and SiCl$_4$:

\[
\text{SiCl}_4 + (\text{C}_6\text{H}_5)_2\text{O} \rightarrow \text{C}_6\text{H}_5\text{Cl} + \text{C}_6\text{H}_5\text{OSiCl}_3
\]

\[
\text{C}_6\text{H}_5\text{OSiCl}_3 + \text{C}_6\text{H}_5\text{MgBr} \rightarrow \text{C}_6\text{H}_5\text{SiCl}_2(\text{OC}_6\text{H}_5) + \text{MgClBr} \text{ etc.}
\]

The synthesis of phenylchlorosilanes may be effected by the action of a suspension of phenylmagnesium chloride in xylene on SiCl$_4$.

Preparation of Phenylchlorosilanes in a Xylene Medium. On the action of a so-
olution of chlorobenzene in xylene on magnesium shavings in the presence of tetraethoxysilane, ethyl bromide, and ethyl ether (1% of the mixture), phenylmagnesium chloride is formed. The optimum synthesis is at a temperature of 120°C. The phenylmagnesium chloride reacts with the calculated quantity of SiCl₄ at room temperature. The mixture is then gradually heated until the organomagnesium compound disappears. The phenylchlorosilanes are distilled under reduced pressure or are extracted and then rectified. The total yield of phenylchlorosilane is 60-70% of theoretical, and phenyltrichlorosilane in the principal reaction product. When ether solutions of p-methoxy- and p-ethoxylmagnesium bromides react with a benzene solution of SiCl₄, the corresponding aryltrichlorosilanes are formed. The yield is 20-45% of theoretical.

Vol'nov and Reutt (Bibl.10) conducted the reaction between SiCl₄ and acetylenemagnesium bromide, prepared by the Iotsich method (without using ether):

\[
\begin{align*}
\text{C}_2\text{H}_5\text{Br} + \text{Mg} & \rightarrow \text{SiCl}_4, \\
\text{C}_2\text{H}_5\text{MgBr} + \text{HC}≡\text{CH} & \rightarrow \text{HC}≡\text{CMgBr} + \text{C}_2\text{H}_6, \\
3\text{HC}≡\text{CMgBr} + \text{SiCl}_4 & \rightarrow (\text{HC}≡\text{C})_3\text{SiCl} + 3\text{MgClBr}
\end{align*}
\]

The reaction of acetylenemagnesium bromide with SiCl₄ is completed when a mixture is heated on a water bath for 3 to 6 hours. The authors did not isolate the product in the pure state, but subjected it to hydrolysis, after first washing out the magnesium chlorobromide:

\[
2(\text{HC}≡\text{C})_2\text{SiCl} + \text{H}_2\text{O} \rightarrow (\text{HC}≡\text{C})_3\text{SiOSi(\text{C}≡\text{C})}_3 + 2\text{HCl}
\]

The hexaacetylenedisiloxane obtained as a result of the hydrolysis is a crystalline product with the melting point 19-20°C.

The di-magnesium derivatives of the alkylhalides or aryldihalides (Bibl.11) can react with SiCl₄ to add one or two silicon atoms, forming either linear compounds or heterocyclic compounds containing magnesium.

The linear compounds form rigid molecules, for example the di-magnesium derivative of p-dibromobenzene.
In the case where the molecule of the dimagnesium derivative does not have a rigid structure, the process proceeds with the formation of a compound containing silicon in the ring. Dimagnesium dibromopentane, for instance, reacts in such a way:

\[
\text{BrMg(gCH}_2\text{)}_2\text{MgBr} + \text{SiCl}_4 \rightarrow \text{H}_2\text{C} - \frac{\text{SiCl}_2}{\text{H}_2\text{C}} + 2\text{MgClBr}
\]

The dimagnesium derivative of acetylene does not react with SiCl₄ (Bibl.12).

**Preparation of Cyclopentamethylenedichlorosilane.** In a round bottom flask 61 g of magnesium shavings are placed, and 2 liters of ether are poured in; 278 g of 1,5-dibromopentane, to which a very small amount of ethyl iodide has been added to accelerate the reaction, is gradually added with stirring. On the completion of the reaction, the mixture is heated under a reflux condenser for 3 hours, then it is cooled, and a solution of 170 g of SiCl₄ in 200 ml of ether is rapidly poured into the flask. The mixture is stirred for 1 hour, and is then decanted. The ether is evaporated and the residue is rectified. The reaction product, cyclopentamethylenedichlorosilane, boils at 165-175°C.

The alkylchlorosilanes react with organomagnesium compounds according to the reaction described for the reaction with SiCl₄. Two-stage alkylation is necessary in the preparation of dialkyldichlorosilane containing branched radicals, and also of substituted silanes containing unlike radicals attached to the silicon atom.

The velocity of reaction is determined not only by the activity of the organomagnesium compounds, but also by the type and number of the organic radicals in the original alkyl-(aryl)-chlorosilane. The velocity of the reaction is considerably lowered by the increasing length of the carbon chain of the organic radical. Thus, for example, when 0.5 mol of trimethylchlorosilane, 0.5 mol of triethylchlorosilane, and 0.5 mol of ethylmagnesium bromide reacts together, trimethylethylsilane and tetraethoxysilane are formed in the molar proportions of 2 : 1, which is evidence...
that the reaction of ethylmagnesium bromide with trimethylchlorosilane proceeds at a rate twice as high as it does with triethylchlorosilane. Propylmagnesium bromide with the same mixture of triethylchlorosilane and trimethylchlorosilane, forms trimethylpropylsilane (and traces of triethylbutylsilane).

The presence of radicals of higher molecular weight in the molecules lowers the velocity of the reaction with an organomagnesium compound still more. The branched and cyclic radicals exert a particularly powerful influence. For example (Bibl.14), on the action of an excess of an ether solution of isobutylmagnesium chloride on a benzene solution of isobutyltrichlorosilane, it is possible to obtain only diisobutylidichlorosilane, and even that in a yield not over 20% of the theoretical. The reaction of triphenylchlorosilane with phenylmagnesium bromide takes place only at a temperature of 180°C.

The cyclohexyl group causes even greater steric hindrance. The reaction between phenyltrichlorosilane and cyclohexylmagnesium bromide for 3 to 4 hours at 180°C leads to the replacement of only two chlorine atoms (Bibl.15):

$$C_6H_5SiCl_3 + 2C_4H_{11}MgBr \rightarrow C_6H_5(C_4H_{11})_2SiCl + 2MgClBr$$

At a high temperature, as a result of the oxidation of the organomagnesium compound, phenyldicyclohexylcyclohexyloxyllsilane is formed:

$$2C_4H_{11}MgBr + O_2 \rightarrow 2C_4H_{11}OMgBr$$

$$C_4H_{11}OMgBr \cdot C_4H_6(C_4H_{11})_2SiCl \rightarrow C_6H_5(C_4H_{11})_2SiOC_6H_{11} + MgClBr$$

When the reaction is conducted in a stream of nitrogen, phenyldicyclohexylsilane is formed. It has not been possible to introduce a third cyclohexyl group into the molecules under any conditions at all. Ethylmagnesium bromide reacts with phenylcyclohexylbromosilane when heated for three hours at 180°C, according to the equation:

$$C_6H_5(C_4H_{11})_2SiBr + C_4H_6MgBr \rightarrow C_6H_5(C_4H_{11})_2SiC_6H_5 + MgBr_2$$

All the above facts evidence the substantial influence of steric hindrance on the process of the reaction between alkylchlorosilanes and organomagnesium compounds.
The organic radicals, attaching to a silicon atom and screening the other bonds of that silicon atom, exert a decisive influence on the behavior of the molecule as a whole, giving it a relative stability to the action of chemical reagents.

We note still another phenomenon which is not merely of theoretical interest but also of practical importance. When chlorosilanes react with alkylmagnesium bromide, there is sometimes an exchange of the halogen atoms, as a result of which alkylbromosilanes may be found in the reaction product. For example (Bibl.16), the action of 18.35 mols of an ether solution of ethylmagnesium bromide on 24 mols of dimethyl-dichlorosilane, results in the formation of 8.33 mols of dimethylethylchlorosilane, 0.723 mol of dimethyldiethylsilane, and 1.506 mol of dimethylethylbromosilane which indicates that the following reaction takes place:

\[
\begin{align*}
\text{CH}_3\text{SiCl}_2 + \text{CH}_3\text{MgBr} & \rightarrow \text{CH}_3\text{CH}_2\text{SiCl}_2 + \text{CH}_3\text{MgCl}.
\end{align*}
\]

There are grounds for asserting that such an exchange of halogens is characteristic for the reactions of organomagnesium compounds with many alkyl-(aryl)-chlorosilanes, as well as with SiCl\textsubscript{4}. The reaction of halogen exchange proceeds more intensely at an elevated temperature. The difficulties of isolating certain products in the individual form are obviously connected with this reaction.

When a method is selected for synthesizing alkyl-(aryl)-chlorosilanes containing different organic radicals attached to a single silicon atom, a considerable number of factors must be borne in mind: the different reactivity of different organomagnesium compounds with respect to the -Si-Cl bond, the screening action of the inserted radicals on the remaining -Si-Cl bonds, the possibility of the halogen exchange reaction, the difficulties of separating the individual intermediate products, and, finally, the difficulty of preparing the starting organomagnesium compounds. For example, the processes of methylation should be, as far as possible, avoided, using methylchlorosilanes prepared by the direct method instead. Further, in certain cases, in the phenylation of methyltrichlorosilane, to obtain a high yield of
the phenylmethyl derivative, it is more convenient to convert the starting product, prepared by the direct method, into the substituted ester, by the action of absolute alcohol. In this case, the process of phenylation proceeds well in a single stage without the use of ether:

\[
\begin{align*}
\text{CH}_2\text{SiCl}_4 + 3\text{C}_6\text{H}_5\text{OH} & \rightarrow \text{CH}_3\text{Si(OC}_2\text{H}_5)_3, \\
\text{C}_6\text{H}_5\text{I} + \text{Mg} + \text{CH}_2\text{Si(OC}_2\text{H}_5)_3 & \rightarrow \text{CH}_3\text{C}(\text{C}_6\text{H}_5)\text{Si(OC}_2\text{H}_5)_3 + \text{C}_6\text{H}_6\text{OMgCl}
\end{align*}
\]

Another example is the synthesis of phenylethylidichlorosilane. It is possible, in principle, to conduct this process, either by ethylation of phenyltrichlorosilane, or by phenylation of ethyltrichlorosilane. When the reaction is conducted according to the former pattern, however, the following complications arise:

1. It is difficult to prepare phenyltrichlorosilane from \( \text{SiCl}_4 \) in sufficiently high yield; 2. the operation of separating the high-boiling products is complicated (phenyltrichlorosilane at a boiling point of 200°C, while phenylethylidichlorosilane boils at 230°C).

It is therefore more advisable to conduct the process according to the second scheme:

\[
\text{C}_6\text{H}_5\text{SiCl}_4 + \text{C}_6\text{H}_5\text{MgCl} \rightarrow \text{C}_6\text{H}_5\text{C}(\text{C}_6\text{H}_5)\text{SiCl}_3 + \text{MgCl}_2
\]

**Preparation of Phenylethylidichlorosilane (Bibl.17).** To 100 g of ethyltrichlorosilane, an ether solution of phenylmagnesium bromide, prepared by reacting 17 g of magnesium with 122 g of bromobenzene, is added. The mixture is stirred for 2 hours at room temperature, after which, for completion of the reaction and in order to convert the precipitate of magnesium chlorobromide into the crystalline state, the mixture is heated on a water bath. The precipitate is removed by filtration or extraction, the ether is distilled off, and the residue is distilled under reduced pressure, at 50 mm. The yield of phenylethylidichlorosilane is 40% of theoretical.

The process may also be conducted by reacting ethyltrichlorosilane with an equimolecular amount of phenylmagnesium chloride without using ether.

In selecting the conditions of the synthesis, and also if it is not necessary
to separate the individual products, the synthesis of chlorosilanes containing two Unlike organic radicals may be accomplished. This is done by the action of a solution of two organomagnesium compounds on $\text{SiCl}_4$, or on the action of a mixture of $\text{SiCl}_4$ and two halogen derivatives on magnesium. In this way, for example, phenylethylidichlorosilane can be prepared.

$$\text{SiCl}_4 + \text{C}_2\text{H}_5\text{Cl} + \text{Et}_2\text{Br} + 2\text{Mg} \rightarrow \text{C}_2\text{H}_5\text{C}_2\text{H}_5\text{SiCl}_2 + \text{MgCl}_2 + \text{MgBr}_2$$

The reaction product contains various alkyl- and arylchlorosilanes, and it is an exceptionally difficult task to separate the mixture into the individual compounds.

When trichlorosilane reacts with organomagnesium compounds, the Si-H bond is in all cases maintained, and the reaction products are either alkylchlorosilanes, $\text{HSiR}_3\text{Cl}_{1-x}$, or alkylsilanes, $\text{HSiR}_3$.

**Alkylation and Arylation of Trichlorosilane (Bibl.18).** 1. To 50 ml of a solution of 175 g of methylinmagnesium bromide in ethyl ether, under cooling with brine and stirring, a solution of 60 g of trichlorosilane in 150 ml of ether is gradually added. The reaction product is acidified with sulfuric acid, the organic layer is separated, and the ether and trimethylsilane are distilled off on the water bath. The trimethylsilane may then be separated from the ether by rectification in a low-temperature column. Its boiling point is 9-11°C.

2. To 135.5 g of trichlorosilanes dissolved in 100 ml of ether, under cooling with ice, a solution of 2.5 mols of ethylmagnesium bromide in 100 mols of ether is added. The mixture is heated 4 hours; the precipitate is separated, and the ether is distilled off. Rectification yields 39 g of ethylidichlorosilane, (boiling point 74.5-75.5°C) and 30 g of diethylchlorosilane, (boiling point 99-100°C). The higher alkylidichlorosilanes, up to octadecylidichlorosilane, may be prepared in a similar way.

3. A solution of 6 mols of phenylmagnesium bromide in ether is added to 6 mols of trichlorosilane at -50°C. The mixture is gradually warmed to room temperature, and the ether is distilled off. The liquid is then separated from the precipitate.
by vacuum distillation to 165°C (5 mm). Rectification yields 188 g of phenyldichlorosilane, boiling point 98°C (51 mm), as well as diphenylchlorosilane, boiling point 140-145°C (7 mm).

4. A mixture of 0.6 mol of benzylmagnesium bromide in ether solution and 0.3 mol of trichlorosilanes is allowed to stand 17 hours at room temperature, and it is then heated 8 hours on a water bath. Filtration and rectification yield 28.2 g of dimethylchlorosilane, boiling point 156-161°C (6 mm).

Reaction of 0.3 mol of benzylmagnesium chloride with 0.3 mol of trichlorosilane under similar conditions yields 11.7 g of benzylidichlorosilane.

Under the action of organomagnesium compound on hexachlorodisilane and hexachlorodisiloxane, the replacement of the halogens is complete, while the Si-Si or Si-O-Si bonds are preserved (Bibl.19). In this way, hexaphenyldisilane in 40% yield and hexatolyldisilane in 30% yield may be prepared from hexachlorodisilane. When smaller quantities of the alkyl-(aryl)-magnesium chloride are used in the reaction, products of incomplete substitution, alkylchlorodisilanes, may be prepared. In contrast to hexachlorodisilane, when hexabromodisilane reacts with organomagnesium compounds, only derivatives of monosilanes are formed, alkylbromosilanes or tetraalkylsilanes.

When a solution of ethylmagnesium bromide acts on hexachlorodisilane, from 1 to 6 chlorine atoms may be replaced by ethyl radicals.

**Preparation of Ethylchlorodisiloxanes.** To prepare compounds of the desired degree of substitution, ethylmagnesium bromide in 25% excess (over the theoretical amount) is added to a solution of 1 mol of hexachlorodisiloxane in 1 liter of ether. The mixture is heated 3-6 hours, after which the residue is filtered off and the filtrate is rectified. Depending on the amount of ethylmagnesium bromide taken in the reaction, products of substitution of 1, 2, 3, and 4 chlorine atoms in the hexachlorodisiloxanes are obtained in 40, 87, 85, and 78% of the theoretical yields, respectively.
Pentaethylchlorodisiloxane may be prepared in 12% yield from triethyltrichlorodisiloxane.

\[
(C_2H_5)_3Si(O)(SiC_2H_5)_2 + 2C_2H_5MgBr \rightarrow (C_2H_5)_4Si(OSi(C_2H_5)_2)C_2H_5 + 2MgClBr
\]

The process is completed when the mixture is heated 10-12 hours.

On the reaction between 2.4 mols of methylmagnesium chloride, 0.1 mol of methylmagnesium iodide, and 1 mol of hexachlorodisiloxane, dimethyltetrachlorodisiloxane is formed in yield of 56% of the theoretical.

\[
CH_3SiCl_2 + 2CH_3MgCl \rightarrow CH_3SiCl_3OSiCH_3 + 2MgCl_2
\]

When 2.85 mols of phenylmagnesium bromide reacts with 1 mol of hexachlorodisiloxane, diphenyltetrachlorodisiloxane is formed. The yield is 17.5% of theoretical. When an excess of phenylmagnesium bromide is used, hexaphenyldisiloxane may be prepared in a yield 40% of the theoretical.

**Preparation of Alkyl-(Aryl)-Chlorosilanes by Means of Organolithium Compounds**

The preparation of alkyl- and (aryl)-chlorosilanes by means of organolithium compounds is the most universal and flexible method of synthesis. The high cost of lithium makes it difficult to use the method on a large scale, but in some cases it is indispensable in laboratory practice. The reaction between the silicon halides and organolithium compounds proceeds easily and in high yield even in those cases when alkylation by the aid of organomagnesium compounds cannot be effected, owing to steric hindrance and the inadequate activity of the organomagnesium compounds. The reaction of alkylation by organolithium compounds differs favorably from the alkylation reactions using sodium, as well, since the former makes good control of the process of synthesis possible.

Organolithium compounds (Bibl. 20) are most often prepared by the action of metallic lithium on an alkyl halide:
Better yields of lithium alkyls are obtained when alkyl chlorides are used (except for methyllithiums, which is prepared from methyl iodide), while the better yields of aryllithium compounds are obtained when arylbromides are used. The reaction between lithium and an alkyl chloride proceeds in the presence of ether, petroleum ether, or cyclohexane, while the reaction with an aryl bromide takes place only in an ether medium. Owing to the exceptional sensitivity of organolithium compounds to the action of atmospheric oxygen, all work with them is done only in an atmosphere of nitrogen. We present examples of the preparation of alkyl- and arylchlorosilanes by the aid of organolithium compounds (Bibl.21, 22).

Preparation of Triphenylchlorosilane. A stream of dry nitrogen is thoroughly blown for 2 hours through a flask provided with a stirrer and mercury seal. Then 120 ml of absolute ether is introduced, followed by 6.6 g of finely ground lithium (see below for the technique of grinding). The stirrer is started, and the small amount (1.5-2 ml) of bromobenzene, out of the total quantity of 62.7 g necessary for the reaction, is poured into the reaction flask with stirring. If the reaction does not begin, the flask is slightly heated on the water bath until the exothermic process does begin. The bromobenzene is now diluted with 120 ml of ether and introduced into the flask over the period of about 1 hour (the reaction is conducted at the boiling point of ether), after which the mixture is heated for an hour, and is then filtered under pressure of dry nitrogen. The phenyllithium solution so obtained is added with stirring to 18 g of SiCl₄ dissolved in 30 ml of ether, and the mixture is heated 2 hours on the water bath. The reaction product is separated by filtration followed by rectification. If the reaction mixture is subjected to hydrolysis, triphenylsilanol can be obtained in a yield of 97% of the theoretical.

Technique of Grinding Metallic Lithium. Mineral oil, purified by sulfuric acid and activated charcoal, is heated 24 hours with metallic sodium at 250°C. The
sodium is removed and the oil is purified a second time. Metallic lithium is introduced into the purified oil, the oil is heated to a temperature of 250°C, and is stirred by a rapidly rotating wire stirrer. After the lithium has been ground, the oil is cooled, and the lithium powder so obtained is removed, while the oil is washed with ether. The lithium so comminuted can maintain its activity only for a few hours and only if kept in a nitrogen atmosphere.

By the aid of organolithium compounds it is possible to prepare tertiary butyl trichlorosilane and dibutyldichlorosilane, which cannot be prepared with organo-magnesium compounds, and also triisopropylsilane, which is difficult to prepare in that way.

It was not possible to prepare tert-tributylchlorosilane, even when a mixture of tert-dibutylchlorosilane and tert-butyllithium is heated at 160°C.

Preparation of Tertiary Butyltrichlorosilane. For the preparation of tert-butyllithium, 3.5 g of lithium, ground by the technique above described, is placed in a reaction bath together with 0.1 g of magnesium powder. Into the flask are now poured 150 ml of petroleum ether, after which 27 ml of tert-butyl chloride is added, with stirring, over a period of 6 hours. The yield of tert-butyllithium is 50% of theoretical. When the butyllithium so obtained is added to a solution of SiCl₄ in petroleum ether, and the mixture is heated on the water bath tert-butyltrichlorosilane is formed. The yield of the product does not exceed 55% of the theoretical (based on the butyllithium taken). Tertiary butyltrichlorosilane is a substance crystalline substance which readily sublimes, and melts at 98-99°C.

Tert-butyltrichlorosilane can be prepared by another method in better yield. By this method, metallic lithium is rolled by special rollers, under a layer of mineral oil, into thin foil, which is cut into pieces 1 cm² in size. The oil is poured off and the lithium is washed with ether. Pentane, treated with sulfuric acid with stirring for three days, is used as a solvent for this synthesis. Before use, the pentane is distilled, and the fraction boiling at 35-36°C, is used for the synthesis.
Freshly distilled tert-butylchloride is used for the synthesis; boiling point 50.0°C, refractive index $n_0^{20} = 1.3850$.

In a 1-liter 3-neck flask, 15.5 g of lithium foil (prepared as described above, which has not come in contact with air) and 375 ml of pentane, are placed. The mixture is heated to boiling, after which a tenth part of a solution of 92.5 g of tert-butylchloride in 300 ml of pentane is introduced into the flask. After the beginning of the exothermic reaction, the source of heat is withdrawn from the flask. The remainder of the solution of tert-butyl chloride is added with vigorous stirring over a period of 6 hours. After the addition has been completed, the reaction mixture is heated for a further period of 2 hours. The yield of tert-butyllithium is from 60 to 75%. To a cool solution of tert-butyllithium, 170 g of freshly distilled SiCl$_4$ is added; the mixture is heated for an hour, after which the reaction product is separated by decantation, extraction, and distillation. The yield of tert-butyldichlorosilane is 75% of theoretical, and the boiling point is 132°C (730 mm).

**Preparation of Tertiary Dibutylchlorosilane.** A solution of 0.72 mols of tert-butyllithium in 750 ml of pentane is placed in a flask serving as the retort for a rectification column and provided with a stirrer. To the solution, 135 g of tert-butyldichlorosilanes is added, and the mixture is heated 4 days, gradually distilling off the pentane at the same time. At the end of the process, the temperature in the reaction flask is 70°C. After the end of the reaction, 500 ml of pentane is introduced into the flask, together with 52 g of SiCl$_4$ to decompose the unreacted butyllithium. The mixture is stirred for an hour, after which the liquid is decanted and rectified. At 190°C (729 mm), 90.3 g of tert-butyldichlorosilane is collected.

**Preparation of Isopropylchlorosilanes.** The reaction between 6.8 g of SiCl$_4$ and 0.2 mol of isopropyllithium in 250 ml of petroleum ether, under the conditions described above, yields 5.8 g of isopropyltrichlorosilane, or 68% of theoretical.

On the reaction of isopropyllithium with trichlorosilane, the replacement of 1, 2, 3 chlorine atoms also takes place. In the latter case, at a temperature of
-5°C to -10°C, a solution of 1.5 mol of isopropyllithium in 1.5 l ether is added to
a solution of 46 g of trichlorosilane in 100 ml of ether. When the introduction has
been completed, the mixture is held for 15 hours at room temperature, and then for
21 hours at the boiling point of ether. On hydrolysis of the reaction mixture, which
takes place when it is poured onto a mixture of ice and sulfuric acid, a mixture of
diisopropylsilanol in 11% yield and tetraisopropylsilanediol in 42% yield is formed.

When trichlorosilane reacts with an organolithium compound, the Si-H bond may be
preserved, which indicates the relatively lower reactivity of the hydrogen attached
to the silicon with respect to the organolithium compounds, by comparison with the
chlorine attached to the silicon. Under more severe conditions, however, the hydro-
gen attached to the silicon is able to react with organolithium compounds to form
lithium hydride and an alkylsilane.

Alkylation by the aid of lithium may also be conducted in a single stage.

**Preparation of a Mixture of Butylchlorosilanes.** To a mixture of 100 ml of ether
and 2.6 g of butyl bromide, 3.47 g of lithium is added, after which a solution of
42.5 g of SiCl₄ in 38.6 g of butylbromide is also added. The mixture is heated on
the water bath for 5 hours, after which the butyltrichlorosilane may be separated by
extraction and rectification, or it may be hydrolyzed.

When SiCl₄ reacts with a large excess of cyclohexyllithium, the only product of
the reaction is tricyclohexylchlorosilane.

**Preparation of Tricyclohexychlorosilane.** To lithium foil under a layer of pe-
troleum ether, 95 g of cyclohexyl chloride is added gradually over a period of 4
hours. The reaction begins on heating, and then continues owing to self-heating.
To the solution of the organolithium compounds so obtained, a solution of 17 g of
SiCl₄ and 50 ml of petroleum ether is gradually added with stirring and cooling with
ice. After standing over night, the precipitate is filtered off, and the excess of
organolithium compound is decomposed with 6 N HCl. The organic layer is separated,
dried over calcium chloride, and the solvent is distilled off, giving a viscous oil,
which is crystallized from glacial acetic acid, and is recrystallized from petroleum ether. The product so obtained, tricyclohexylchlorosilane, has a melting point of 101-102°C.

Tricyclohexylchlorosilane does not react with methylmagnesium iodide nor with methyllithium, even when an ether or toluene solution of a mixture of the components is boiled. When tricyclohexylchlorosilane is heated with metallic sodium in a medium of toluene, to boiling, no reaction is observed, either.

Under the action of lithium-aluminum hydride on tricyclohexylchlorosilane, it can be reduced to tricyclohexylsilane.

Preparation of Tricyclohexylsilane. To tricyclohexylchlorosilane, dissolved in ether, an excess of lithium-aluminum hydride in ether solution is added dropwise. After the reaction mixture has been boiled for half an hour, the ether is distilled off, and the residue is dissolved in petroleum ether. The solution is heated, and the residue of unreacted hydride and mineral salts is filtered off. The solvent is then distilled off.

The yield of the product is 80% of theoretical.

Tricyclohexylsilane, \((\text{C}_6\text{H}_{11})_3\text{SiH}\) is an oily liquid; boiling point 183-185°C (9 mm); refractive index \(n^25_D = 1.5132\). It does not crystallize, even when cooled with a mixture of solid CO\(_2\) and alcohol.

Tricyclohexylsilane is easily brominated in the cold in a solution of CCl\(_4\); yielding tricyclohexylbromosilane in quantitative yield; melting point 112-113°C, when tricyclohexylsilane is boiled 2 hours with a solution of iodine in CCl\(_4\), tricyclohexyliodosilane is formed, which is crystallized from petroleum ether and recrystallized from ethanol; melting point 97-98°C. The yield is 52%. Tricyclohexyliodosilane decomposes easily in the light, liberating iodine.

When tricyclohexylsilane is boiled with an excess of 5% alcoholic KOH, tricyclohexylsilanol, \((\text{C}_6\text{H}_{11})_3\text{SiOH}\), is formed. To the reaction mixture, to separate this product, an equal volume of water is added, and the \((\text{C}_6\text{H}_{11})_3\text{SiOH}\) is then thrown
down as a precipitate. The product is crystallized from ethyl ether and recrystallized from petroleum ether; melting point 176-177°C. The yield is 87%. When tricyclohexylsilanol is boiled with acetic anhydride, tricyclohexylacetoxysilane, \((\text{C}_6\text{H}_{11})_3\text{SiOOCCH}_3\), is formed, and is precipitated from the reaction mixture when it is cooled to 0°C under vigorous stirring. To purify the product it is washed with ethanol; melting point 82-83°C. Yield, 80% of theoretical.

By the aid of organolithium compounds it is possible to prepare alkyl-(aryl)-chlorosilanes containing the most varied organic groups, for example, 1-methoxy-4-bromophenyltrichlorosilane, etc. Organolithium compounds are very often irreplaceable reagents for the synthesis of tetra-substituted silanes.

**Preparation of Alkyl-(Aryl)-Chlorosilanes by the Aid of Organosodium Compounds**

The method of preparing alkyl- and arylchlorosilanes by the aid of organosodium compounds is of considerably less value than the methods described above. This is because this reaction is very difficult to control. The liberation of a considerable amount of energy on the reaction of an organosodium compound with a halosilane at the first Si-Cl bond encourages the reaction at all the remaining -Si-Cl bonds, so that, for example, for \(\text{SiCl}_4\) the process is completed almost quantitatively with the formation of the tetra-substituted product \(\text{SiR}_4\). When the usual measures of precaution are observed, and when an excess of chlorosilane is used, a certain amount of alkylchlorosilanes can be obtained as a result of the reaction. Thus, for instance, on the reaction between sodium, \(\text{SiCl}_4\), and ethyl bromide, the ratio between diethyldichlorosilane, tristhylchlorosilane, and tetraethylsilane is 1 : 1 : 2 (Bibl.23).

When phenylsodium acts on \(\text{SiCl}_4\), phenyltrichlorosilane can be obtained in low yield. However, in evaluating the method of preparing alkyl-(aryl)-chlorosilanes by the aid of organosodium compounds, it must be borne in mind that the process gives satisfactory yields only with the simplest aromatic radicals; the alkylsilanes
usually give a low yield, (even when all the reaction products, both alkylchlorosilanes and tetra-substitution products are taken into account). If, however, the molecule of the halogen derivative has a long or highly branched chain, or a functional group in the phenyl nucleus (nitrochlorobenzene, methoxychlorobenzene, etc), it is not possible to run the reaction at all. Certain unsaturated derivatives, for instance sodium acetylide, likewise do not react at all.

The synthesis of the alkyl- and arylchlorosilanes by means of organosodium compounds has no practical application.

**Preparation of Alkyl-(Aryl)-Chlorosilanes by the Aid of Organomercury and Organozinc Compounds**

Phenyltrichlorosilane was first prepared (Bibl.24) by prolonged heating of 100 g of diphenylmercury with 50 g of SiCl₄ in a sealed tube at 300°C:

\[
\text{SiCl}_4 + \text{Hg(C}_6\text{H}_5)_2 \rightarrow \text{C}_6\text{H}_5\text{SiCl}_3 + \text{C}_6\text{H}_5\text{HgCl}
\]

Tolyltrichlorosilane can be similarly prepared. At the present time, this method is of no practical importance, owing to the difficulties of conducting the process, the low yields, and the toxicity of mercury.

Dimethylmercury, trimethylaluminum, and dimethylzinc do not react with SiCl₄ (Bibl.25).

Diethylchlorosilane may be prepared by means of diethylzinc:

\[
\text{SiCl}_4 + \text{Zn(C}_2\text{H}_5)_2 \rightarrow (\text{C}_2\text{H}_5)_3\text{SiCl}_2 + \text{ZnCl}_2
\]

**Preparation of Diethylchlorosilane (Bibl.26).** Zinc dust, containing 0.5-1% of copper, is washed with concentrated HCl and water, and is dried in a stream of hydrogen; 16 g of the zinc dust so treated is placed in a flask, provided with a stirrer, together with 50 g of ether. While stirring the contents of the flask, a mixture of 20 g of ethyl iodide and 11.5 g of SiCl₄ is gradually introduced. The mixture is heated to the boiling point over a period of 8 hours, after which the
diethyldichlorosilane may be either separated by extraction and rectification, or hydrolyzed; in this case liquid polydiethyldisiloxane is formed. The yield is 72% of theoretical. Diethyldichlorosilane is also prepared by the reaction of 1 mol of SiCl₄ with 2 mols of ethylzinc bromide over a period of 6 hours at the boiling point of ethyl ether. Ethylzinc bromide is formed on heating zinc dust, activated with HCl with ethyl bromide in the presence of ether for 36 hours. In this case, 85% of the zinc is dissolved.

**Direct Synthesis of Alkyl-(Aryl)-Chlorosilanes**

The reaction between elementary silicon and a gaseous alkyl halide at an elevated temperature, is extremely important for the synthesis of organosilicon compounds. In the ideal case, the process may be represented as follows:

\[
\begin{align*}
2\text{Si} + 4\text{RCI} & \rightarrow \text{RSiCl₄} + \text{R₂SiCl₂} \\
\text{Si} + 2\text{RCl} & \rightarrow \text{R₂SiCl₂}
\end{align*}
\]

the first reactions being of principal importance, and the second subordinate. In practice, however, the reaction between silicon and an alkyl halide yields a large number of the most varied products, liquid (R₂SiCl₂, R₃SiCl, R₃SiCl₂, SiCl₄, H₃SiCl₂), gaseous (RH, R-R, H₂) and solid (carbon).

This process may be conducted without using a catalyst, but in this case the reaction proceeds slowly, and the relative importance of the pyrolytic processes is great, so that the products of the reaction consists mainly of the chlorosilanes with a high chlorine content (SiCl₄, RSiCl₃, R₃SiCl₂). The use of a copper catalyst (or also of a silver catalyst for the arylchlorosilanes) accelerates the reaction, and allows its temperature to be lowered and brings the process close to the ideal mechanism described by reactions (1) and (2).

The reaction between silicon and an alkyl halide is an exothermic process.

The principal raw material for the synthesis of alkylhalosilanes is silicon or
ferrosilicon containing not less than 90% of silicon. The best results are obtained when silicon of the first grade (mark KR-1) is used, which usually contains 99.5% of silicon. Either electrolytic copper or copper prepared by reduction from its sales is used as a catalyst. The starting alkyl chloride must not contain traces of moisture, alcohols, or other impurities.

A number of methods for preparing the mixture of silicon and catalysts, the contact mass, are described in the literature. We give three of the most important methods:

1. Fusion of copper with silicon in a reducing medium, followed by rapid cooling of the alloys so prepared to prevent segregation of the copper. When the alloy is cooled, according to the type of contact apparatus, it is ground either into lumps 10-15 mm in size, or is ground into dust on a ball mill.

2. A mixture of finely ground silicon and copper powders is compressed into tablets under a pressure of the order of 5000 kg/cm², and tablets are reduced in an atmosphere of hydrogen at a temperature up to 1060°C to increase the catalytic activity of the mass.

3. Mixing the powdered silicon and copper and cuprous chloride, compression into tablets, drying, and reduction of the tablets at 300°C according to the formula:

\[ \text{Si} + 2 \text{CuCl}_2 \rightarrow \text{SiCl}_4 + 4\text{Cu} \]

The conduct of the reaction between the alkyl halide and the contact mass involves no difficulties and can be accomplished in any laboratory.

Method of Conducting the Direct Synthesis of Alkyl- and Arylhalosilanes. Into a glass, porcelain or steel tube (best of copper-lined) 50 mm in diameter and 1 m long, 500 g of the contact mass ground into lumps 10 mm in size is charged. The tube is heated from without in a tubular muffle furnace. The gaseous alkyl halide enters the contact tube from a cylinder through a receiver and washer with sulfuric acid, and a flow meter. The liquid halogen derivatives, for instance chlorobenzene, enter
from a dropping funnel through a pressure tube about 0.5 m high to overcome the insignificant pressure in the apparatus (for this purpose the upper part of the dropping funnel may also be connected with the contact tube). Before the beginning of the process, the contact mass is dried in a stream of inert gas at a temperature of 200°C until all traces of moisture in the waste gases have disappeared (tested by passing the gases through anhydrous copper sulfate). If the contact mass has been prepared from cuprous chloride, its temperature is brought up to 300°C, and in 1 minute an exothermic process of reduction takes place, liberating SiCl₄. After the reduction a stream of inert gas, is blown through the contact mass.

The contact mass is heated to the temperature required for the synthesis, after which a stream of gaseous alkyl halide is passed through the mass at the rate of about 30 liter/hour, or of liquid alkyl halide at a rate of 20 g/hour. The reaction products, condensing in the water-cooled condenser, flow off into the receiving flask. If the synthesis is conducted with a gaseous alkyl halide, the receiver is provided with a reflex condenser cooled by ice or brine. The waste gases pass into a condenser cooled by a mixture of acetone and solid carbon dioxide, to condense the unreacted alkyl halide.

The mechanism of the reaction between the alkyl halide and the silicon has not yet been definitively established. The following course of the process is the most probable (Bibl.27, 28). The metallic copper reacts with the alkyl chloride at the temperature of synthesis, forming alkyl copper chloride:

\[
\text{Cu} + \text{RCI} \rightarrow \text{RCuCl}
\]

which, in the presence of silicon, is capable of dissociating into the radicals:

\[
\text{RCuCl} \rightarrow \text{Cu} + \text{R} + \text{Cl}^-
\]

The free radicals so formed react with silicon:
The free valences of the silicon may then, depending on the reaction conditions, be saturated by organic radicals, chlorine, or by the hydrogen formed as a result of pyrolytic processes.

At the temperature of synthesis, the free radicals are subjected to pyrolysis, but also enter into the most diverse combinations, as a result of which a number of hydrocarbons as well as hydrogen and carbon, are formed. The latter accumulates in the contact mass in the form of coke, which is one of the causes for the reduction in the activity of the contact mass, of the increased synthesis temperatures, of the intensification of the pyrolytic processes, and, ultimately, of the poorer composition of the condensate. The spent contact mass usually contains considerable amounts (6-10%) of carbon in the form of soot, whose presence makes the spent contact mass readily inflammable in air at room temperature.

The lower the temperature of synthesis, the lower the intensity of the pyrolytic processes, and the closer the course of the process to the ideal. For this reason, one of the main conditions of successful conduct of the process of direct synthesis is providing, at all points of the contact mass, the minimum temperature at which the reaction between silicon and the alkyl halide begins. This temperature is different for the different alkyl halides or aryl halides.

**Preparation of Methylchlorosilanes**

The reaction between silicon and methyl chloride, in the absence of a catalyst (Bibl.28) proceeds at a temperature of 285°C, and the quantity of the reaction products in this case (the condensate in the receiving flask) does not exceed 57% of the weight of the methyl chloride passed through, while the average number of radicals attached to the silicon atom is only 0.56, that is, the reaction product consists mainly of SiCl₄ and methyltrichlorosilane. These data speak for the completely unsatisfactory course of the process and of the abundant liberation of gaseous
products of pyrolysis.

One of the principal forms of the contact mass is an alloy of copper and silicon. The results of work with an alloy containing 50% of copper and 50% of silicon at a temperature of 312°C, has been described (Bibl.2). The description unfortunately indicates the yield of condensate erroneously (almost double the theoretical), which makes any evaluation of the data difficult. The ratio between the number of radicals and the number of silicon atoms, according to the analytical results for the hydrolysis product, is rather high, 1.8.

These figures, however do not sufficiently characterize the effectiveness of the contact mass in the form of an alloy. Using an alloy containing only 20% copper, the reaction could probably be conducted at a lower temperature, thus assuring a higher yield of the desired products.

A contact mass prepared by reduction of a mixture of cuprous chloride and silicon, possesses high activity (Bibl.28). The reaction between the reduced mass and methyl chloride at 300°C leads to the formation mainly of dimethyldichlorosilane, but after 25% of the silicon has been used up, the content of chlorosilanes with a larger number of chlorine atoms in the condensate increases. After 60% of the silicon has been used up, the average composition of the condensate collected throughout the entire process, is as follows: dimethyldichlorosilane, 42.1%; methyltrichlorosilane, 36.8%; methyldichlorosilane, 11.8%.

Under certain conditions, this method allows us to conduct the process at a lower temperature, yielding a condensate containing 75% of dimethyldichlorosilane. In this case, about 80% of the silicon is used.

A certain modification (Bibl.29) of this method of briquetting a mixture of copper and silicon in the powdered form namely compression under a pressure of 5-7 tons/cm², makes it possible to conduct the process under completely different conditions and with different equipment. The compressed mass is broken up into small pieces and is reduced in a contact apparatus at 275-300°C. It is found that the re-
action with methyl chloride takes place in this case at 290-310°C, and from the contact mass prepared from 85 g of silicon and 15 g of cuprous chloride, 153 g of condensate is formed in 90 hours (using up about half of the silicon). Thus the amount of condensate is somewhat more than half the amount of the methyl chloride passed through. In another experiment, at 295-305°C, (at a rate of flow of 6.2 g of methyl chloride an hour) 160.4 g of condensate was obtained in 71 hours, that is, less than half the weight of the methyl chloride passed through. The percentage composition of the condensate in these two experiments was as follows:

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyldichlorosilane</td>
<td>21.7</td>
<td>39.6</td>
</tr>
<tr>
<td>Methyltrichlorosilane</td>
<td>39.8</td>
<td>35.0</td>
</tr>
<tr>
<td>Methyldichlorosilane</td>
<td>16.0</td>
<td>8.7</td>
</tr>
</tbody>
</table>

These data cannot be recognized as satisfactory. On observing certain conditions of synthesis, and with the proper arrangement of the process, the yield of condensate may considerably exceed that stated, and the average content of dimethyldichlorosilane in the condensate will amount to 50%, using up 70% of the silicon (Bibl.30).

Another patent contains references (Bibl.31) to the possibility of using, as a catalyst, copper oxide or copper powder oxidized on the surface, but the results adduced by the author are entirely unsatisfactory.

One of the most widely used forms of the contact mass (Bibl.30), which are given in the present literature, is a mixture of finely ground silicon and copper powders, compressed under a pressure of about 5 ton/cm² and reduced in a stream of hydrogen at a temperature up to 1060°C. This type of contact mass is probably what is meant by the general term copper-silicon mass; this term is often used in patents, without indicating the method of preparing the mass. The copper content in the mass varies over a wide range, from 2 to 45%; the optimum ranges from 20 to 25%.

The literature throws very little light on the apparatus setup of the direct synthesis. The following indication is of interest (Bibl.30). On reaction of methyl chloride with the contact mass prepared from 20 kg of silicon and 2.2 kg of copper powder (obviously prepared by the above described method) in a "oil-heated
band-type reactor, 81 kg of condensate was obtained in 124 hours from 77 kg of methyl chloride (that is, 103% on the basis of the methyl chloride consumed), and this condensate contained 63.6% of dimethyl dichlorosilane, 11.8% of methyltrichlorosilane, and 25% of a fraction boiling up to 66°C. In another experiment, the same quantity of contact mass and 67 kg of methyl chloride yielded only 55 kg of a condensate containing 59.3% of dimethyl dichlorosilane. The results of the first experiment speak for the high activity of the contact mass and are the best results published in the literature. The high percentage of silicon utilized is worthy of notice (4 kg of condensate from each kg of silicon, which corresponds to the utilization of almost 90% of the silicon), as well as the high process productivity obtained in working with such a contact mass (0.8 kg of condensate day per kg of silicon in the contact mass).

In a number of patents (Bibl.32) the possibility of conducting a fluid process is proposed in general terms: the contact mass in the form of dust is ejected by a jet of methyl chloride into the reactor, whence the products of reaction pass into an expander, then into a dust separator, and then come for separation. The recycling of the methyl chloride and the contact mass powder is provided for. The condensate contains 57% of dimethyl dichlorosilane. It is stated that the process proceeds under a pressure of 3-4 atm at 330-370°C. The principal advantages of the process is obviously the high productivity of the contact mass. Finally, one of the works, (Bibl.31) indicates the preparation of large quantities (hundreds of kg) of methylchlorosilanes in a "vertical stationary reactor 100 mm in diameter".

The dilution of the methyl chloride by an inert gas (Bibl.30) (5-20% of nitrogen) encourages an increase in the dimethyl dichlorosilane content of the condensate to 86.5% as against 73.5% without such dilution (the type of contact mass and the process conditions are not indicated by the authors). The hydrogen dilution gives the increased content of chlorosilanes containing the Si–H bond in the condensate (the content of methyl dichlorosilane rises to 17%).
The trimethylchlorosilane content of the condensate under ordinary conditions does not exceed 5%. The trimethylchlorosilane content can be increased in the condensate by adding aluminum or zinc to the contact mass (Bibl.33). Thus on addition of aluminum powder (5% of the contact mass by weight)* and conduct of the synthesis at 300-350°C, the trimethylchlorosilane content of the condensate is increased to 10%. If the amount of aluminum** in the contact mass is increased to 10%, then the trimethylchlorosilane in the condensate rises to 20%. By adding 20% of zinc powder to the contact mass and conducting the synthesis at 330-350°C, the trimethylchlorosilane content of the condensate is likewise increased to 20%. The patent unfortunately fails to indicate the content of the main product of the reaction, dimethyldichlorosilane, in the condensate, which is probably sharply reduced when the process is run under these conditions. The conditions given in the patent can therefore not be recognized as optimum. It is, however, possible to find conditions under which this method will make it possible to increase the trimethylchlorosilane content without appreciable reduction of the dimethyldichlorosilane content.

There is a reference (Bibl.33) to the possibility of diluting the methyl chloride, before its introduction into the contact apparatus, with 5-35% of chlorine by volume (the composition of the condensate is not stated). This is obviously advisable when methyltrichlorosilane is desired as a product, since, in the presence of chlorine, the synthesis of methyltrichlorosilane can proceed without loss of methyl chloride:

\[ \text{Cl}_2 + \text{CH}_3\text{Cl} + \text{Si} \rightarrow \text{CH}_3\text{SiCl}_3 \]

The yield of dimethyldichlorosilane under these conditions is probably sharply lower.

The introduction of methyl chloride with an admixture of HCl into the contact

* The aluminum powder must have a particle size such that it will pass a No. 200 sieve.

** In this case the aluminum powder must pass a No. 100 sieve.
apparatus has been patented (Bibl.31); but the data given in the patent are entirely inadequate for determining the composition of the reaction product or the yield of methylchlorosilane. Thus the patent states that on passage of methyl chloride with an admixture of 2% of HCl over the contact mass at 370°C, the condensate is converted after hydrolysis into a solid colorless resin. From these data no conclusions as to the composition of the products can be drawn. Obviously the main product under these conditions is methyltrichlorosilane, but at this temperature, even without using HCl, the main product of the reaction should be methyltrichlorosilane.

Better results are obtained (Bibl.33) when finely ground copper powder (oxidized from the surface) with particle sizes of a few microns, is used as the catalyst. The copper particles are surrounded by an extremely thin oxide film which prevents further oxidation. The oxide film is so thin that its presence can be established only by the aid of X-ray analysis. It is stated that on passage, through a contact mass consisting of 50 kg of silicon powder and 5.55 kg of copper powder in a "strip type reactor heated by an oil jacket", of 155.25 kg of methyl chloride over a period of 124 hours, 164.25 kg of condensate is obtained, being 106% of the weight of the methyl chloride, and containing 63.6% of dimethyldichlorosilane, 11.8% of methyltrichlorosilane, and 25% of a fraction boiling below 66°C.

The high percentage of utilization of silicon in the contact mass must be noted. It yields 3.3 kg of condensate from 1 kg of silicon, which corresponds to the utilization of about 72% of the silicon. The high productivity of the contact mass should also be noted (0.6 kg of condensate per kg of contact mass per day), which is probably assured by the appropriate design of the contact apparatus. In another experiment, the yield of condensate amounted to only 82% of the quantity of the methyl chloride passed through, and the dimethyldichlorosilane content was only 59.3%.

The words "band type reactor" in the patent probably mean a contact apparatus with the band mixer described in another patent (Bibl.34). Figure 28 gives a diagram of such a contact apparatus.
Preparation of Methylchlorosilanes in a Band Type Reactor. The process of reaction between methylchloride and the contact mass is conducted in the reaction chamber I into which the contact mass is charged through the stub pipe 2. The mass is stirred by the band mixer 3, attached to the shaft of the contact apparatus and brought into rotary motion by means of the motor 4. The band of the mixer is arranged in the form of a screw. In plan, the band consists of a ring whose area is

Fig. 28 - Contact Apparatus for Conduct of Direct Synthesis:
1 - Reaction chamber; 2 - Admission pipe for contact mass; 3 - Band mixer; 4 - Motor; 5 - Admission pipe for methyl chloride; 6 - Jacket; 7 - Filter; 8 - Condenser; 9 - Outlet pipe for uncondensed gases; 10 - Receiver; 11 - Discharge pipe for spent contact mass

Fig. 29 - Diagram of Installation for Direct Synthesis by the Fluid Process:
1 - Methyl chloride supply pipe; 2 - Tube for contact mass; 3 - Reaction chamber; 4 - Cooling chamber; 5 - Partition; 6 - Tube for recycling contact mass; 7 - Additional methyl chloride induction pipe; 8 - Tube for supplying fresh contact mass; 9 - Cyclone fan; 10 - Receiver for spent contact mass; 11 - Filter; 12 - Condenser; 13 - Receiver
55–60% of the cross sectional area of the contact apparatus. When the shaft rotates, the band rises above that part of the contact mass located near the walls of the contact apparatus; while the mass located at the center, near the shaft (outside the area of the ring of the band), descends. Thus, on a relatively slow rotation of the mixer, thorough mixing of the contact mass takes place. The methyl chloride arrives in the reaction chamber 1 through the stub pipe 5. In this chamber the temperature necessary for synthesis is maintained by feeding a heat-carrier into the jacket 6 of the contact apparatus. The reaction mass need be heated only during the initial stage of the process; after the beginning of the reaction, the heat-carrier serves to carry off the heat liberated during the reaction. The reaction products, passing through the filter 7 and the condenser 8, are collected in the receiver 10, while the uncondensed gases are withdrawn through the pipe 9 for deep chilling and for catching the methylchloride. The contact mass spent during the process of synthesis, is discharged from the contact apparatus through the stub pipe 11.

According to patent data (Bibl.35), the optimum particle size for a contact mass in the form of an alloy ranges from 74 to 105 microns. The proportion of particles smaller than 44 microns must not exceed 15%, and that of particles larger than 149 microns must not exceed 5%. Direct synthesis by the fluid process can probably be most conveniently conducted with such a contact mass.

Figure 29 gives a diagram of a fluid-process installation.

Preparation of Methylchlorosilanes in a Fluid-Process Installation. The reaction between methyl chloride and the contact mass takes place in the vertical tube 3. The methyl chloride, obviously first heated to the reaction temperature, is fed through the pipe 1, and is drawn over the contact mass entering through the pipe 2. The reaction chamber may consist either of the pipe shown on the figure, or a cylinder of larger cross section in which the reaction mass is mixed. The process may be conducted either at normal or elevated pressure. The necessary temperature is maintained by the heat liberated during the reaction. The mixture passes from the
reaction chamber into the cooling chamber 4, which is provided with the partition 5, where the main part of the unreacted copper-silicon alloy powder is separated and flows along the inclined bottom of the cooling chamber into the tube 6, whence it passes through a slide gate into the tube 2 and is recycled to the reaction chamber 3. The circulation of powder is accelerated when a certain quantity of methyl chloride or nitrogen is introduced through the pipe 7. The fresh powdered contact mass enters through the tube 8. From the chamber 4, the mixture passes into the cyclone fan 9, where the finely dispersed spent powder is separated. The spent contact mass is collected in the receiver 10 and can be activated by oxidation (decarbonisation), and is then recycled to the synthesis. After separation of the reaction products from the dust, they arrive in the filter 11, and then in the condenser 12, where the methylchlorosilanes are condensed, and are then collected in the receiver 13. According to the data of the patent, at a temperature of 330-370°C and a pressure of 3.5 atm, the condensate will contain 57% of dimethyl dichlorosilane.

The installation can have a higher productivity. If, in selecting the optimum process conditions, the dimethyl dichlorosilane content of the condensate can be held stable within the limits of 50-57%, the design of the installation must be regarded as good (provided an adequate percentage of silicon is utilised). Unfortunately the patent does not give exhaustive data on the operation of the installation.

Other data on the design of contact devices for direct synthesis have not been published, except for a short statement (Bibl.34) that considerable quantities of methylchlorosilanes (hundreds of kilograms) have been produced in "vertical stationary reactors 100 mm in diameter".

There are references to the possibility of direct synthesis of methylchlorosilanes in the presence of HCl (Bibl.98).

Preparation of Methylchlorosilanes in the Presence of Hydrogen Chloride (Bibl.98). Anhydrous HCl is passed at 370°C into a glass tubular furnace in which a 1:1 copper-silicon alloy is placed, and then a mixture consisting of 1 part by
volume of HCl and 50 parts by volume of methyl chloride is passed over a period of 8 hours through the furnace.

The reaction products are condensed at \(-80^\circ C\), and are then hydrolysed by a mixture of ice, water, and ether. The polymethyilsiloxanes so prepared are condensed on heating into viscous or solid resins. When a mixture of methyl chloride and HCl in the ratio of 7 : 1 by volume is passed in over a period of 1 hour at 360\(^\circ C\), and then in the ratio of 20 : 1 over a period of 1 hour, similar products are formed.

When methyl chloride is passed over silicon powder for 24 hours at 380\(^\circ C\) at the rate of 80 ml/min, a condensate of boiling point 55-80\(^\circ C\), containing trimethylchlorosilane, dimethyldichlorosilane, and methyltrichlorosilane, is formed. When a mixture of methyl chloride and HCl in the proportions of 1 : 1 by volume is passed through under these same conditions, similar results are obtained. When a mixture of CH\(_3\)Cl and HCl in the proportions of 20 : 1 by volume is passed, the yield of polyethylsiloxane is 4 times as great as those obtained in the preceding experiments.

Separation of the reaction products of silicon with methyl chloride. Most of the byproducts of the reaction between silicon and methyl chloride are gases and are easily separated from the condensate of methylchlorosilanes. The methyl chloride is usually separated from the gas mixture by deep cooling (\(-40^\circ C\)), and is condensed together with the residue of the methylchlorosilanes that have passed through the water cooler, while the gas mixture is recycled to the reactor. The remaining gases consist mainly of ethane, hydrogen, and ethylene. The losses, when the process functions satisfactorily, do not exceed 7-10%.

An insignificant part of the pyrolysis products consist of liquids which are condensed together with the methylchlorosilane and hinder their separation in the pure state.

The condensate, together with the dissolved methyl chloride, also contains the following compounds:

<table>
<thead>
<tr>
<th>Compound</th>
<th>B.P.</th>
<th>Quant.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trimethylchlorosilane</td>
<td>52</td>
<td>3-5</td>
</tr>
<tr>
<td>Methyltrichlorosilane</td>
<td>40-6</td>
<td>5</td>
</tr>
<tr>
<td>Silicon tetrachloride</td>
<td>57-6</td>
<td>Traces</td>
</tr>
</tbody>
</table>

F-TS-9191/V 424
Trimethylchlorosilane \((\text{CH}_3)_3\text{SiCl}\) ............ \(57.7\) \(3-5\)
Methyltrichlorosilane \((\text{CH}_3)\text{SiCl}_3\) .................. \(66.1\) \(10-40\)
Dimethyldichlorosilane \((\text{CH}_3)_2\text{SiCl}\) .................. \(70.2\) \(30-70\)
2-Methylpentane \(\text{C}_{6}\text{H}_{14}\) .................................. \(60.4\) \(0.2-0.3\)
3-Methylpentane \(\text{C}_{6}\text{H}_{14}\) .................................. \(65.3\) \(0.2-0.4\)
2-Methylhexane \(\text{C}_{7}\text{H}_{16}\) .................................. \(90.1\) \(0.1\)
Ethylene Chloride \(\text{CH}_2\text{CHCl}_2\) ......................... Traces

* Content fluctuates sharply according to the conditions of synthesis.

An admixture of \(\text{SiCl}_4\), boiling point \(57.6^\circ\text{C}\), and paraffin hydrocarbons with six carbon atoms, can often be detected in the trimethylchlorosilane, boiling point \(57.7^\circ\text{C}\) (Bibl.36). The appearance of these compounds indicates the unsatisfactory regulation of the process temperature. At a high temperature, there is thermal decomposition of the methyl chloride, forming, hydrocarbons or chlorinated hydrocarbons for instance ethylene chloride. A disproportionately high ratio of the chlorine content to the content of the uncleaved methyl groups, results in an increased yield of \(\text{SiCl}_4\). The further cleavage of the methyl groups, accompanied by the liberation of elementary hydrogen, leads to the formation of compounds with the Si-H bond, for instance, of trichlorosilane, boiling point \(32^\circ\text{C}\), or methyldichlorosilane, boiling point \(40.6^\circ\text{C}\). Although the dimethyldichlorosilane is sometimes also contaminated with hydrocarbons, the greatest difficulties of all are encountered in the purification of the trimethylchlorosilane, since it forms azeotropic mixtures with \(\text{SiCl}_4\) and 2-methyl- and 3-methylpentanes (the boiling point of the azeotropic mixture is \(57.6^\circ\text{C}\)). Besides this, ethylene chloride, boiling point \(54.7^\circ\text{C}\), also forms a binary azeotrope with trimethylchlorosilane and with \(\text{SiCl}_4\), and possibly also a ternary azeotrope with these same compounds.

The separation of the mixture of methylchlorosilanes and their preparation in the pure form is a very complicated problem. In practice, the most complex process is the separation of a pure dimethyldichlorosilane, entirely free from all traces of methyltrichlorosilane. Pure dimethyldichlorosilane is necessary for the preparation of a high molecular polydimethylsiloxane, elastomer. Dimethyldichlorosilane does not form azeotropic mixtures with any of the products of the reaction, and therefore...
it may be separated by rectification on a column of adequate size. The complete separation of methyltrichlorosilane, which boils only 2°C below dimethyldichlorosilane, may be accomplished in a column of 60-70 theoretical plates with a sufficiently high reflux ratio.

The construction of bubble-cap laboratory columns of this type has been described in adequate detail (Bibl.37). The process of rectification of methylchlorosilanes does not differ from that of multi-component organic mixtures with boiling points of the components of the mixture close together. The fact that the vapor of the methylchlorosilanes must not come in contact with the moisture of the atmosphere must be borne in mind. The purity of the dimethyldichlorosilane must be carefully verified by checking its boiling point, its density, and its content of titratable chlorine. The chlorine content of sufficiently pure dimethyldichlorosilane does not exceed 55.1%.

After the separation of the intermediate fraction at about 70°C has been completed, the rectification process cannot be significantly forced by reducing the reflux ratio. It is possible in this case that the product will be contaminated by traces of methylhexane, which boils at a temperature over 90°C, and by the products of hydrolysis of CH₃SiHClOSiCH₃HCl. The presence of traces of hydrocarbon in the dimethyldichlorosilane does not interfere with the subsequent hydrolytic processes, since the high-boiling products of hydrolysis are easily separated from admixtures of volatile hydrocarbons.

The separation of pure methyltrichlorosilane is also a complicated operation, since it is difficult to remove the traces of dimethyldichlorosilane from this product. But this is not as important as in the separation of pure dimethyldichlorosilane. For practical purposes the fraction of methyltrichlorosilane boiling in the range 65-67°C and containing 70% chlorine instead of the theoretical 71.1%, can be used. Methyltrichlorosilane, just like dimethyldichlorosilane, forms no azeotropic mixture with the other components of the mixture.
It is incomparably more difficult to separate the third main component of the mixture, trimethylchlorosilane. As stated above, the ethylene chloride, SiCl₄, trimethylchlorosilane, 2-methyl-, and 3-methylpentanes, which are present in insignificant amounts in the condensate, all boil in the range 57.4-63.2°C. These products may form the following azeotropic mixtures:

1) SiCl₄, 64.8%, and trimethylchlorosilane, 35.2% - boiling point of mixture 54.7°C;

2) trimethylchlorosilane, 70%, and 2-methylpentane, 30%; boiling point of mixture, 56.4°C;

3) trimethylchlorosilane, 75%, and 3-methylpentane, 25%; boiling point of mixture, 57.3°C;

4) SiCl₄, 63.5%, and ethylene chloride, 36.5%; boiling point of mixture 53°C.

In addition, ternary azeotrope mixtures are probably also formed.

It is practically impossible to separate the pure trimethylchlorosilane completely from the mixture, by rectification alone. But this is not necessary; all that is required is to separate the trimethylchlorosilane quantitatively from the SiCl₄. This operation does not involve any difficulties in principle; the process of separation may be effected either by physicochemical or by chemical methods.

In all cases it is necessary on rectification to separate the fraction containing the trimethylchlorosilane. The separation may be accomplished by azeotropic rectification of the separated fraction with a new component yielding azeotropic mixtures of different boiling points with SiCl₄ and trimethylchlorosilane. The following may be used as such components: acrylonitrile, boiling point 79°C, which forms an azeotropic mixture with 93% of trimethylchlorosilane, boiling point of mixture 57°C; and with 89% of SiCl₄ (boiling point of mixture 51.2%).

Acetonitrile, (boiling point 82°C), forms azeotropic mixtures with 92.6% of trimethylchlorosilane, boiling point of mixture 56°C; and with 90.6% of SiCl₄, boiling point of mixture 49°C.
By chemical separation of a mixture of trimethylchlorosilane and SiCl₄, the trimethylchlorosilane may be isolated in the chemically pure state. The process may be accomplished by two methods:

1. Esterification of the mixture by ethylene oxide, forming a mixture of esters:

\[
\text{SiCl}_4 + 4\text{CH}_2\text{CH}_2\text{O} \rightarrow \text{Si(OC}_2\text{H}_5\text{Cl)}_4
\]

\[
(\text{CH}_3)_2\text{SiCl} + \text{CH}_2\text{CH}_2\text{O} \rightarrow (\text{CH}_3)_2\text{SiOC}_2\text{H}_5\text{Cl}
\]

The trimethyl-β-chloroethoxysilane so formed is easily separated both from hydrocarbons and from the tetra-β-chloroethoxysilane. The trimethylchlorosilane may be obtained by treating this substituted ester with benzoyl chloride:

\[
(\text{CH}_3)_2\text{SiOC}_2\text{H}_5 + \text{C}_6\text{H}_5\text{COCl} \rightarrow (\text{CH}_3)_2\text{SiCl} + \text{C}_6\text{H}_5\text{COOC}_2\text{H}_5
\]

2. By hydrolysis of the mixture, distilling off the pure hexamethyldisiloxane, and then treating it with sulfuric acid and ammonium chloride.

If the synthesis is conducted under sufficiently mild conditions, and the temperature at all points of the contact mass is regulated with sufficient accuracy, no SiCl₄ at all will be formed. This considerably facilitates the process of separating the mixture and makes it possible by only a single rectification to separate the trimethylchlorosilane (56–58°C) completely. This product will be found to be sufficiently pure and can be used for most practical purposes, and in particular, for the preparation of hexamethyldisiloxane.

Preparation of Ethylchlorosilanes

The reaction between ethyl chloride and silicon has not been described adequately in the literature. There is an indication (Bibl.38) that when a contact mass containing 10% of copper is used, and the process is conducted at 300–325°C, a condensate of the following percentage composition is formed: (%)

\[
\begin{align*}
\text{SiCl}_4 & \quad \text{------------------------} \quad 37 \\
\text{Diethylenedichlorosilane} & \quad \text{...........} \quad 26
\end{align*}
\]
When suitable conditions of reaction between the ethyl chloride and the copper-
silicon contact mass are selected, however, it may be conducted at 240-250°C, and in
this case SiCl₄ will be present in the condensate only in insignificant amounts. It
has not been possible to obtain a high diethylidichlorosilane content in the condens-
ate, for the principal reaction product is ethyltrichlorosilane. Ethylidichloro-
silane is also present in significant amounts (Bibl.38).

The mixture may be separated in a rectification column of 25-30 theoretical
plates.

Preparation of Alkylchlorosilanes Containing Unsaturated Radicals (Bibl.39)

Allyl chloride reacts actively with silicon at a temperature of 250°C. The re-
anction is exothermic, and unless the temperature is carefully regulated, it may rise
of itself to 500-600°C. The dilution of the allyl chloride by an inert gas is recom-
mended. In working with a contact mass containing 10% of copper, a condensate con-
taining 40% of low-boiling products of little value (SiCl₄, trichlorosilane, etc),
and 60% of a mixture of allylchlorosilanes may be obtained, from which rectification
yields allyldichlorosilane, C₃H₅SiHCl₂, (boiling point 97°C), allyltrichlorosilane,
C₃H₅SiCl₃, (boiling point 117.5°C), and diallyldichlorosilane, (C₃H₅)₂SiCl₂, (boiling
point 82-84°C at 50 mm). The latter is contained in only insignificant quantities in
the mixture.

In contrast to allyl chloride, vinyl chloride enters only slightly into reaction
with the contact mass, the reaction takes place only at temperatures over 300°C, and
the conversion of the vinyl chloride is slight. From the condensate, vinyltri-
chlorosilane, (boiling point 92°C), and divinylidichlorosilane, (boiling point 118-
119°C), in ratio 1 : 3, may be separated. 1,2-dichlorovinyltrichlorosilane and
2,2-dichlorovinylidichlorosilane are also obtained.
Preparation of Phenylchlorosilanes (Bibl.40)

The reaction between silicon and chlorobenzene differs substantially from its reaction with the alkyl chlorides. The reaction of silicon with chlorobenzene in the presence of a catalyst begins only at 380°C; the optimum synthesis temperature is 400-420°C. In the absence of a catalyst, the process proceeds at a considerably higher temperatures. Thus, for example, when chlorobenzene is passed through ground silicon placed in a contact tube 25 mm in diameter at 680°C for 54 hours, 367 g of condensate is obtained, being 90% of the quantity of chlorobenzene passed in, and containing 17.8% of high-boiling fractions: phenylchlorosilanes, diphenyl, and the product of partial hydrolysis of the phenylchlorosilanes. If the chlorobenzene is passed in together with dry HCl (0.3 mol per mol of chlorobenzene), the synthesis may take place at 550°C, and 9.4 g of phenyltrichlorosilane are obtained from 100g of chlorobenzene.

According to the literature, the best catalyst is a 50% alloy of copper and silicon, oxidized in a stream of air at 300°C for 15 hours. Chlorobenzene containing 0.04% of HCl reacts with such a contact mass at a temperature of 430°C, forming a condensate containing 9-10% of phenyltrichlorosilane and 20-24% of diphenyl dichlorosilane. Benzene and biphenyl are byproducts of the reaction. The mixture also contains insignificant amounts of phenyl dichlorosilane, C₆H₅SiHCl₂, boiling point 173°C. The chlorobenzene content is 50-60%. Calculation shows that to obtain 1 kg of phenylchlorosilanes, 1.5-1.7 kg of chlorobenzene is used; thus the yield is entirely satisfactory.

When a contact mass containing 10% of silver as a catalyst is used, the condensate obtained at 400°C contains 4% of phenyltrichlorosilane, 10% of diphenyldichlorosilane, and about 3% of products boiling above 305°C. After 70 days of operation, the content of phenylchlorosilanes in the condensate falls to 5%, indicating the loss of activity of the contact mass.

The literature data on the preparation of the phenylchlorosilanes, one of the
most important forms of organosilicon monomers, is fragmentary and inadequate. In particular, one of the most important indexes, the percent of utilization of silicon in the contact mass, is nowhere stated. There are reasons for considering that in working with the above described contact masses, this amount is very small, and therefore other forms of contact masses allowing the utilization of 60-70% of the silicon (with a phenyltrichlorosilane content of 15-30% in the condensate) is of practical importance.

The arylhalosilanes are also prepared by the action of an aryl chloride and HCl on alloys of silicon and copper (Bibl.41).

**Preparation of Phenylchlorosilanes.** When chlorobenzene is passed at the rate of 22 g/min for 132 hours through a vertical tubular furnace, 1500 x 44 mm in size, filled with 1300 parts of weight of silicon powder with a fine grind of 325 meshes, and activated in a stream of hydrogen at 1350°C, a condensate with a boiling point above 132°C is formed. It consists mainly of biphenyl and its chlorine derivatives, and contains an insignificant amount of phenylchlorosilanes (1.4%). Similarly, on passing 2710 parts by weight of chlorobenzene and 450 parts by weight of HCl at 490-515°C for 167 hours through such a furnace, 273 parts by weight of a condensate containing about 165 parts by weight of phenyltrichlorosilane, is formed. When chlorobenzene and HCl are passed at the respective rates of 13.8 and 1.92 parts by weight per minute, at 436-445°C, for 116 hours, 116 parts by weight of a condensate consisting mainly of C₆H₅SiCl₃ is formed.

A 2.84% yield of C₆H₅SiCl₃ was attained on passing chlorobenzene and HCl at the respective rates of 13 and 0.43 parts by weight per minute through the furnace for 66 hours at 1000°C. Passage of a mixture consisting of 72 parts by weight of HCl and 1550 parts by weight of C₆H₅Cl at 430-450°C for 72 hours over a copper-silicon alloy in proportions of 1 : 9, yielded 168 parts by weight of a condensate containing 132 parts of C₆H₅SiCl₃. The yield of phenyltrichlorosilane does not exceed 8.8%.
Other Reactions with a Copper–Silicon Contact Mass

Methylene chloride (Bibl.185, I, 2, 33), CH₂Cl₂, reacts with a 10% copper–silicon contact mass at 300°C. The methylene chloride should be diluted with up to 50% of nitrogen for better control of the reaction. The following were isolated from the reaction products:

<table>
<thead>
<tr>
<th>Compound</th>
<th>B.P. in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl₂SiCH₂Cl₂</td>
<td>51–52.5 (10 mm)</td>
</tr>
<tr>
<td>Cl₂SiCl₂SiCl₂</td>
<td>65 (10 mm)</td>
</tr>
<tr>
<td>(Cl₂SiCl₂)ₙ</td>
<td>81–82.8 (M.P.)</td>
</tr>
</tbody>
</table>

The presence of certain higher cyclic methylene chlorosilanes, (Cl₂SiCH₂)ₙ, boiling above 200°C (10 mm) has been established.

Dichloroethane reacts similarly, and the principal reaction product in this case is hexachloroethylenedisilane, Cl₃SiCH₂CH₂SiCl₃; boiling point 92.5–93°C (25 mm); melting point 27–29°C.

There is a statement (Bibl.39) that when the mixture of the vapor of a simple ether and a hydrogen halide react with a copper–silicon contact mass at temperatures of 250–425°C, alkylchlorosilanes are formed. The ratio between the number of radicals and the number of silicon atoms in the reaction product is regulated by the amount of hydrogen halide (from 0.2 to 1 mol per mol of ether). The composition of the reaction product is not indicated.

CCl₄ (Bibl.40) reacts with a 10% contact mass at 200°C to form tetrachloroethylene and hexachlorodisilane (Bibl.40).

Reactions with Other Contact Masses

The chlorosilanes are alkylated (Bibl.43) by alkyl halides in the presence of such metals as aluminum or zinc at temperatures of the order of 300–500°C. The hydrolysis of the products obtained by the reaction of tetrachlorosilane and methyl chloride leads to the formation of a resinous substance resembling the corresponding polyorganosiloxanes. On the reaction of methyltrichlorosilane and methyl chloride
at 450°C, 21% of trimethylchlorosilane, 11% of dimethyldichlorosilane, and traces of methylidichlorosilane are formed. At 350°C, the ratio of the products was somewhat modified; at 400°C, a certain quantity of tetramethylsilane was formed. As a result of the reaction of dimethylchlorosilane with methyl chloride, trimethylchlorosilane in 30% yield is formed. A mixture of dimethyldichlorosilane and ethyl chloride forms dimethylethyldichlorosilanes.

The reaction between dimethyldibromosilane and methyl bromide leads to the formation of trimethylbromosilane.

The hydrogenation of SiCl₄ and certain methylchlorosilanes leads to the replacement of a chlorine atom by hydrogen.

It is believed that this reaction may be represented as follows:

\[
2 \text{Al} + 3 \text{CH}_2\text{Cl} \rightarrow \text{CH}_3\text{AlCl}_3 + (\text{CH}_3)_2\text{AlCl}
\]

\[
7\text{H}_2\text{SiCl}_4 + 2(\text{CH}_3)_2\text{SiCl}_2 \rightarrow 2(\text{CH}_3)_3\text{SiCl} + \text{AlCl}_3
\]

The aluminum encourages the replacement of chlorine in alkylchlorosilanes by organic radicals. It is also able to displace silicon from its compounds:

\[
7\text{H}_3\text{SiCl}_4 + \text{Al} \rightarrow (\text{CH}_3)_3\text{AlCl} + 4\text{SiCl}_3
\]

The literature describes the replacement of halogens attached to the silicon by alkyl radicals at high temperatures (Bibl.44). It was originally found, for the substituted silanes of type RₓSiCl₄-x, where the value of x must be at least equal to 1, that aluminum or zinc were satisfactory catalysts. A mixture of dimethyldichlorosilane and methyl chloride in the proportion 1:1 at 350°C gave a 30% yield of trimethylchlorosilane. When methyltrichlorosilane reacts with methyl chloride at 350°C, 6% of trimethylchlorosilane and 4.5% of dimethyldichlorosilane was obtained. When the temperature was raised to 450°C, the yields were increased to 11% and 21%, respectively. In addition, 3-4% of methylidichlorosilane was obtained. Dimethyldichlorosilane and methyl bromide in molar ratio 2:1 reacted over aluminum at
350°C forming trimethylbromosilane, while dimethyldibromosilane and ethyl chloride yielded dimethylethylchlorosilane. The reaction of methyl chloride with dimethyldichlorosilane in the presence of zinc at 375°C yielded trimethylchlorosilane in 30% yield.

The literature describes a process for the preparation of organosilicon compounds by reacting benzene and trichlorosilane at 750-770°C over a catalyst consisting of fused quartz and small pieces of clay plates. The principal reaction product was phenyldichlorosilane (Bibl.48).

Preparation of Alkylchlorosilanes from Hydrocarbons and Chlorosilanes

In 1935, Shtetter (Bibl.45) described the reaction between SiCl₄ and certain compounds containing a double bond. The process proceeds under a pressure of 10 to 100 atm in the presence of catalysts, aluminum, iron, and certain heavy metal chlorides, as well as mercury oxychloride. According to the data of the author, the process proceeds with formation of products containing only a single Si-C bond. The reaction with ethylene, acetylene, and carbon monoxide may be represented as follows:

\[
\begin{align*}
\text{CH}_2=\text{CH} + \text{SiCl}_4 & \rightarrow \text{CICH}_2\text{CH}_3\text{SiCl}_3 \\
\text{HC}==\text{CH} + \text{SiCl}_4 & \rightarrow \text{CICH}==\text{CHSiCl}_3 \\
\text{CO} + \text{SiCl}_4 & \rightarrow \text{CICOSiCl}_4
\end{align*}
\]

The reaction described by Shtetter is very interesting, but until recently not a single work had been published confirming or elaborating his data. It is only recently, in one of the patents (Bibl.46) that an indication appeared to the effect that SiCl₄ reacts with ethylene in the presence of a mixture of aluminum chloride with mercury oxide or with mercury chloride. The process proceeds under a pressure of 16 atm, at 25-35°C. The authors did not isolate the reaction product, however; all the reaction mixture was hydrolyzed, forming a polymer of the composition \((\text{HOCH}_2\text{H}_4\text{SiO}_{1.5})_x\). The Shtetter synthesis does not seem to us as simple as the patent indicates, and for its successful accomplishment a number of precautions are
obviously necessary.

According to data of Andrianov and Kochkin (Bibl.47), SiCl₄ reacts with a hydrocarbon at a temperature over 450°C:

\[ \text{RH} + \text{SiCl}_4 \rightarrow \text{RSiCl}_3 + \text{HCl} \]

There are statements in patents (Bibl.48) that when a mixture of SiCl₄ and methane is passed over pumice at 500°C, 12.2% of methyltrichlorosilane can be obtained, and that a certain amount of phenyltrichlorosilane is obtained from a mixture of benzene and SiCl₄ at a red heat.

This method at the present time is not of practical importance, since the reaction proceeds at too slow a rate, even at temperatures that lead to appreciable pyrolytic processes.

The difficulties involved in the addition of hydrocarbons to SiCl₄ are probably due to the energetic stability of the Si-Cl bond. The process proceeds in an entirely different way where one of the bonds of the silicon atom is energetically less stable. Many reactions are known (Bibl.49) in which the Si-H bond is broken and an organic radical adds to the silicon atom. The most difficult case is the reaction between trichlorosilane and an unsaturated hydrocarbon. The process proceeds readily in the presence of a peroxide or on irradiation of the reaction mass with ultraviolet light. An advantage of the method is the simplicity of the separation of the reaction mass, since only a single compound is formed during the reaction (Bibl.89).

\[ \text{RCH} = \text{CH}_2 + \text{HSiCl}_3 \rightarrow \text{RCH}_2\text{CH}_3\text{SiCl}_3 \]

Where the olefin molecule has a double bond at the primary carbon atom, the silicon atom adds at this primary atom. In this way a number of alkyltrichlorosilanes of normal or branched structure can be prepared. The reaction with normal olefins usually takes place more easily than with branched olefins. If the double bond of the olefins is in the middle of the molecule, however, the silicon atom
adds to the most electronegative carbon atom.

The optimum ratio is from 0.3 to 0.75 mol of olefin to 1 mol of trichlorosilane, when 0.013 to 0.026 mol of peroxide per mol of trichlorosilane is used. As an example we give the method of preparing octyltrichlorosilanes from 1-n-octene.

Preparation of Octyltrichlorosilane. A mixture of 7.9 g of octene and 135.5 g of trichlorosilane is placed in a flask provided with a stirrer and a reflux condenser connected with a dry ice-acetone trap. To remove the air, dry nitrogen is blown through the flask. The process is conducted under low pressure of nitrogen produced by means of a cylinder and a mercury seal 200 mm high, installed after the trap. After the nitrogen has been passed for 2 hours, the temperature of the mixture rises to 45°C, and a solution of 1.5 g of crystalline acetyl peroxide in 19.1 g of octene is added to the mixture over a period of 2 hours. The mixture is then heated 9 hours at 50-63°C, after which the excess of trichlorosilane is distilled off, and the residue is fractionated under reduced pressure. The yield of octyltrichlorosilane is 80.9 g, which amounts to 99%; boiling point 231-232°C (731 mm).

In the presence of a peroxide under ultraviolet irradiation, the process is conducted at 46-52°C for 24 hours. The yield of octyltrichlorosilane is 31% of the theoretical.

Similar reactions with isobutylene, cyclohexene, 1-pentene and a number of other olefins take place at 70-100°C over a period of not more than 24 hours. The yield as a rule is high: for instance, 2-methyl-1-heptene at 49-58°C for 25 hours gives a yield of 70% of product.

Under ultraviolet irradiation in the absence of peroxide, the yield is usually smaller, and equilibrium is reached more slowly; for instance, in the presence of a peroxide, allyl chloride forms propyltrichlorosilane in 27 hours in 24% yield, while under ultraviolet irradiation without peroxide in 45 hours, the yield is only 8.4%.

The mechanism of the action of a peroxide catalyst is probably as follows. In the first stage, a certain number of free radicals are formed:
The relative weakness of the Si-H bond makes its rupture possible:

\[ \text{HSiCl}_3 + \text{CH}_2 \rightarrow \text{CH}_2 \rightarrow \text{SiCl}_3. \]

The SiCl\(_3^+\) radical reacts with the olefin, adding at the position of the double bond:

\[ \text{RCH} = \text{CH}_2 + \text{SiCl}_3 \rightarrow \text{RCH} - \text{CH}_2 \text{SiCl}_3 \]

after which the complex so formed reacts with a new molecule of trichlorosilane to form a new trichlorosilyl radical:

\[ \text{RCHCH}_2\text{SiCl}_3 + \text{HSiCl}_3 \rightarrow \text{RCH}_2\text{SiCl}_3 + \text{SiCl}_3 \]

This radical again adds to the double bond of the olefin, etc.

The addition reaction between olefins and trichlorosilanes has been studied in detail for olefins of various structures, for example \( \text{RCH} = \text{CH}_2, \text{RCH} = \text{CHR}, \text{R}_2\text{C} = \text{CH}_2 \), \( \text{R}_2\text{C} = \text{CHR}, \text{R}_2\text{C} = \text{CR}_2 \), where \( \text{R} \) is an alkyl or chloroalkyl radical.

When \( \text{R} \) is a radical with a normal chain, for instance methyl, n-amyl, or n-hexyl then alkyltrichlorosilanes are obtained in good yield. But if \( \text{R} \) is a multibranched chain, for instance, tertiary butyl or tetramethylmethane, then the yield of alkyltrichlorosilanes is substantially lowered. The low yield of isobutyltrichlorosilane, may possibly be explained by the fact that owing to the higher volatility of the olefin, the reaction is conducted at low temperature. A peroxide catalyzes this reaction better in ultraviolet light. Under the action of ultraviolet light in the reaction with 2-methyl-2-butene, however, a high yield of the product was obtained. The alkyltrichlorosilanes, under ordinary conditions, are not capable of further reaction with the olefins, and therefore in most cases very pure products are obtained by this reaction. This method therefore has advantages, for the preparation of
the alkyltrichlorosilanes, over the Grignard method and over direct synthesis, both of which yield mixtures of alkylchlorosilanes (Bibl.50).

The synthesis of 1,1,2-trimethylpropyltrichlorosilane from 2,3-dimethyl-2-butene and trichlorosilane is of interest, since the above described methods of preparing tertiary alkylchlorosilanes by using tertiary lithium compounds, which are difficult to prepare in good yield (Bibl.51), are disadvantageous. A comparison of the results of a preliminary study of the reactions between 1-octene and silicon hydrides has shown that trichlorosilane reacts considerably more readily than other silanes.

n-Propyldichlorosilane, on reaction with 1-octene in the presence of diacetyl peroxide, gave a low yield (6%) of propyloctyldichlorosilane, containing admixtures. Triethoxysilane does not react with 1-octene in the presence of all the above mentioned catalysts.

Triethyilsilane does not react with 1-octene in the presence of a peroxide, but under the action of ultraviolet light, it does give a low yield of an impure product. Diethylsilane gave an excellent yield of a product which apparently consisted mainly of diethylctysilane, but it could not be isolated, owing to the small amount of the starting product. SiCl₄ did not react with 1-octene in the presence of a number of catalysts.

The following reactions have been investigated (Bibl.52):

\[
\begin{align*}
\text{CH}_3=\text{CH}_2 + \text{HSiCl}_3 & \rightarrow \text{CH}_3=\text{CHCH}_2\text{SiCl}_3, \\
\text{C}_3\text{H}_7\text{CH} = \text{CH}_2 + \text{HSiCl}_3 & \rightarrow \text{C}_3\text{H}_7\text{SiCl}_3, \\
\text{C}_6\text{H}_{13} + \text{HSiCl}_3 & \rightarrow \text{C}_6\text{H}_{11}\text{SiCl}_3, \\
\text{CH} = \text{CH}_2 = \text{CHCl} + \text{HSiCl}_3 & \rightarrow \text{CH} = \text{CHCH}_2\text{H}_2\text{SiCl}_3, \\
\text{C}_2\text{H}_5\text{CH} = \text{CH}_2 + \text{CH}_3\text{SiHCl}_3 & \rightarrow \text{C}_2\text{H}_5\text{SiCH}_3\text{H}_2\text{Cl}, \\
\text{C}_6\text{H}_{13}\text{CH} = \text{CH}_2 + \text{CH}_3\text{SiHCl}_3 & \rightarrow \text{C}_6\text{H}_{12}\text{SiH}_2\text{Cl}_2, \\
\text{C}_6\text{H}_{13}\text{CH} = \text{CH}_2 + \text{CH}_3\text{SiHCl}_3 & \rightarrow \text{C}_6\text{H}_{12}\text{SiH}_2\text{Cl}_2.
\end{align*}
\]

It is very probable that these reactions might be considered as reactions of free radicals, since the catalysts are peroxides and ultraviolet light.

The literature presents a description of the reactions between silanes and alkyl chlorides in the presence of aluminum chloride (Bibl.53):
\[
\begin{align*}
(C_3H_5)SiH + C_6H_{14}Cl & \rightarrow C_6H_{14} + (C_3H_5)SiCl \\
(C_3H_5)SiH + \underset{CH_2}{\overset{CHCH_2CH_2Cl}{\text{CH}_2}} & \rightarrow C_6H_{14} + (C_3H_5)SiCl \\
(C_3H_5)SiH + \underset{CH_2}{\overset{CHCH_2CH_2Cl}{\text{CH}_2}} & \rightarrow (CH_3)CHCH_2CH_2CH_2 + (C_6H_{14})SiCl
\end{align*}
\]

These reactions are very exothermic.

There are indications that trimethylchloromethylsilane was converted under the action of aluminum chloride into dimethylethylchlorosilane (Bibl.95), and that besides this a side reaction took place, the disproportionation of dimethylethylchlorosilane, as a result of which a mixture of trimethylchlorosilane, diethyldichlorosilane and triethylchlorosilane was formed.

The monoalkyl-substituted ethylenes react with trichlorosilane in the presence of benzoyl peroxide under ultraviolet irradiation. This reaction did not take place with triethoxysilane, triethylsilane, nor with SiCl₄ (Bibl.55).

The process may also be conducted under pressure, without using a catalyst (Bibl.54), but in this case it proceeds at higher temperatures. Thus, when a mixture of trichlorosilane with octadecene is heated for 2.5 hours at 300°C, octadecyltrichlorosilane is obtained; the yield is 94% of theoretical.

At a temperature above the decomposition point of an olefin, its addition to trichlorosilane involves certain side processes; thus, for example, trichloroethylene and trichlorosilane at 490°C form 2,2-dichlorovinyltrichlorosilane (Bibl.55).

\[
\begin{align*}
\text{Cl}_2\text{C}=\text{CHCl} + \text{HSiCl}_3 & \rightarrow \text{Cl}_2\text{CH}=\text{CHCISiCl}_3 \\
\text{Cl}_2\text{CH}=\text{CHCISiCl}_3 & \rightarrow \text{HCl} + \text{Cl}_2\text{C}=\text{CHSiCl}_3
\end{align*}
\]

The formation of the \( \beta, \beta \)-dichloro-isomer (instead of the \( \alpha, \beta \)-isomer, as that author assumed), indicates that this process proceeds according to the mechanism we have presented, instead of being preceded by the cleavage of HCl and the formation of dichloroacetylene, which reacts with the trichlorosilane.
Preparation of 2,2-dichlorovinyltrichlorosilane. Into a glass tube 9 mm in diameter and 180 mm long, an inert filler, which helps to improve heat-transfer, is charged. A mixture of 35 g of trichloroethylene and 25 g of trichlorosilane is introduced at a temperature of 490°C for 3 hours into the tube. From the 50 g of reaction product, on rectification, 5.3 g of unreacted trichlorosilane and 29.4 g of dichlorovinyltrichlorosilane are obtained on rectification; boiling point of the latter is 52°C (8 mm). The yield is 87.7%. The quantity of HCl formed during the reaction (7 g), somewhat exceeds the theoretical (6.5 g). When the reaction is conducted in a sealed tube in the presence of a peroxide catalyst at a low temperature, the process gives a very low yield.

Dichlorovinyltrichlorosilane, as a compound with a double bond, can in turn add a still another molecule of trichlorosilane:

\[
\text{Cl}_2\text{C} = \text{CH} \text{SiCl}_3 + \text{SiHCl}_3 \rightarrow \text{Cl}_2\text{SiCl}_2\text{CH}_2\text{SiCl}_3
\]

It has been noted (Bibl. 46), that trichlorosilane can add to the double bonds of rubber. On heating a mixture of trichlorosilane and a benzene solution of rubber at 300°C under a pressure of 60 atm for 16 hours, a product containing from 1 to 2 mols of trichlorosilane at the double bond has been obtained, which on hydrolysis and condensation forms a film with good adhesion to glass.

Tetrachloroethane and trichloroethane are able to react at a temperature of 500°C according to the following mechanism:

\[
\text{Cl}_2\text{CH} = \text{CHCl} \rightarrow \text{ClICH} = \text{CCl}_3 + \text{HCl} \\
\text{ClICH} = \text{CCl}_3 + \text{HSiCl}_4 \rightarrow \text{Cl}_2\text{CH} = \text{CHSiCl}_4 \\
\text{Cl}_2\text{CH} = \text{CHSiCl}_4 \rightarrow \text{Cl}_2\text{C} = \text{CHSiCl}_3 + \text{HCl}
\]

Obviously the first reaction takes place at the lowest velocity, since on the reaction between trichlorosilane and trichloroethylene, the amount of dichlorovinyltrichlorosilane is 87.7%, while the yield of this substance from tetrachloroethane is only 15%.
The process is accomplished by passing a mixture of 26.0 g of trichlorosilane and 26.5 g of trichloroethylene through a 9-mm contact tube at 500°C for 95 min.

When propylacetylene reacts with trichlorosilanes, 1-pentenyl-1-trichlorosilane is formed (Bibl.55, 99).

The reaction takes place according to the formula:

\[ C_6H_5C\equiv CH + HSiCl_3 \rightarrow C_6H_4CH\equiv CHSiCl_3 \]

Preparation of 1-pentenyl-1-trichlorosilane (Bibl.55). A mixture of 271 g of trichlorosilane and 12.1 g of benzoyl peroxide is placed in an enameled autoclave. To the mixture 34 g of propylacetylene dissolved in 50 g of trichlorosilane is added. The mixture is then heated to 80°C and held at this temperature 52 hours. Fractionation of the reaction products yields mainly unreacted trichlorosilane, together with 10.8 g of 1-pentenyl-1-trichlorosilane; boiling point 85°C (80 mm).

Dichloroacetylene (easily explodes) reacts in the presence of acetyl peroxide with trichlorosilane in a sealed tube at 0°C for 65 hours, forming 3,8-dichlorovinyltrichlorosilanes.

\[ C_2H_3CC\equiv CCl + HSiCl_3 \rightarrow CICH\equiv CClSiCl_3 \]

The yield of the product is 28%.

Trichlorosilane may be alkylated in other ways than the action of unsaturated hydrocarbons. Under the proper conditions (true, with low yields) it reacts with alkyl halides and even hydrocarbons (Bibl.48, 56). Thus when a mixture of 1 mol of ethyl chloride and 1 mol of trichlorosilane reacts in a nickel bomb for 22 hours at 312-316°C under a pressure of 130 atm, 0.21 mol of ethyltrichlorosilane and 0.66 mol of SiCl₄ is formed. A mixture of 1 mol of bromobenzene and 0.85 mol of trichlorosilane, when passed through a quartz tube filled with clay tablets, at 750-770°C, reacts to form insignificant amounts of phenyltrichlorosilane.
Preparation of Alkylhalosilanes by the Diazol Method

Haloalkylhalosilanes, containing a halogen atom in the α-position, may be prepared by the reaction of tetrahalosilanes with aliphatic diazo compounds.

Using the diazo method developed by A.N. Nesmeyanov (Bibl.57) for the synthesis of organo-element compounds, Yakubovich and Ginzburg (Bibl.58) first established the possibility of preparing organosilicon compounds from silicon halides and aliphatic diazo compounds.

Under ordinary conditions the silicon halides (SiF₄, SiCl₄, SiBr₄) energetically decompose aliphatic diazo compounds (diazomethane, diazoethane), but the formation of organosilicon compounds is not observed. Organosilicon compounds can be obtained with these reactions only as a result of the interaction of the reagents at low temperatures. The best yields (up to 65%, based on the diazo compound) are obtained at temperatures from -70°C to -60°C. The reactions proceed according to the formulas:

\[
\begin{align*}
\text{SiCl}_4 + \text{CH}_3\text{N}_2 & \rightarrow \text{CICH}_2\text{SiCl}_3 + \text{N}_2 \\
\text{SiCl}_4 + \text{CH}_2\text{C}\text{H}_2\text{N}_2 & \rightarrow \text{CH}_3\text{CHSiCl}_3 + \text{N}_2 \\
\text{SiBr}_4 + \text{CH}_3\text{N}_2 & \rightarrow \text{BrCH}_2\text{SiBr}_3 + \text{N}_2
\end{align*}
\]

The compound formed may in turn be alkylated by diazo compounds:

\[
\begin{align*}
\text{CICH}_2\text{SiCl}_3 + \text{CH}_3\text{N}_2 & \rightarrow \text{CICH}_2\text{SiCl}_3 + \text{N}_2 \\
\text{(CICH}_2\text{)}_3\text{SiCl}_2 + \text{CH}_3\text{N}_2 & \rightarrow \text{(CICH}_2\text{)}_3\text{SiCl}_2 + \text{N}_2
\end{align*}
\]

Usually a mixture of products is formed, and the predominance of any one of them depends on the proportions of the starting reagents. As the alkyl radicals accumulate, however, further alkylation is impeded. The trialkylchlorosilanes, for instance trimethylchlorosilane, enter with particular difficulty into reaction with diazomethane. Triethylchlorosilane is not alkylated at all by diazomethane, even on prolonged contact.

In those cases where the reaction between halosilicon compounds and diazo compounds proceed slowly, catalysts may be used, such as bronze, anhydrous copper sulfate, and the like, which strongly accelerate the reaction between these reagents.
without exerting any substantial influence on the yield of organosilicon products.

$\text{SiF}_4$ is not alkylated by aliphatic diazo compounds, although it does energetically decompose them. The silicon bromides are alkylated with considerably more ease than the chlorides, and in better yield. In this case the di- and trialkylhalosilanes $R_2\text{SiBr}_2$ and $R_3\text{SiBr}$ are formed with appreciably greater ease than the monoalkylhalosilanes.

In this way, various $\alpha$-haloalkyl-derivatives of silicon may be prepared. $\text{ClCH}_2\text{SiCl}_3$, $(\text{ClCH}_2)_2\text{SiCl}_2$, $(\text{ClCH}_2)_3\text{SiCl}$, $\text{CH}_3(\text{ClCH}_2)\text{SiCl}_2$, $\text{CH}_3\text{CHClSiCl}_3$, $(\text{BrCH}_2)\text{SiBr}_3$, $(\text{BrCH}_2)_2\text{SiBr}_2$, $(\text{BrCH}_2)_3\text{SiBr}$ have been prepared by this method.

The mechanism of this reaction is apparently as follows: the molecule of silicon halide, on meeting the unstable molecule of the aliphatic diazo compounds, causes it to decompose, liberating nitrogen:

$$\text{CH}_2\text{N}_2 \longrightarrow \text{CH}_2 + \text{N}_2$$

and forming an alkylene radical. The latter in turn either polymerizes or reacts with the molecule of silicon halide.

It is well known that in the series $\text{SiF}_4$, $\text{SiCl}_4$, $\text{SiBr}_4$, the energy of the Si-X bond decreases markedly (from 143 kcal for Si-F to 69 kcal for the Si-Br bond). Accordingly the possibility of the Si-C bond being formed may be facilitated on transition from silicon fluoride to silicon bromide, which does in fact happen.

The role of the catalyst (copper etc) reduces down to the acceleration of the process of decomposing the diazo compound into the alkylene and nitrogen, if this decomposition proceeds with insufficient energy under the action of the molecule of silicon halide itself.

The practical value of the reaction for use in industry is reduced owing to the need of conducting it at a low temperature.
Preparation of Alkylchlorosilanes by the Vapor-Phase Method (Bibl.59)

The reaction between an alkyl halide, an alkylchlorosilane, and the metal is of great practical interest, since it allows the use of relatively less valuable alkyltrichlorosilanes for the synthesis of the di- and trialkyltrichlorosilanes. The reaction between methyltrichlorosilane, methyl chloride and aluminum powder may serve as an example of this reaction:

$$3CH_3SiCl_3 + 3CH_3Cl + 2Al \rightarrow 3(CH_3)Cl_iSiCl_3 + 2AICl_3$$

$$3(CI_3j)SiCl_2 + 3CH_3Cl + 2Al \rightarrow 3(CH_3)2SiCl + 2AlCl_3$$

Method of Preparing Alkylchlorosilanes by Vapor-Phase Alkylation (Bibl.59).

Methyl chloride from a cylinder enters the mixer, where it is bubbled through liquid chlorosilane and entrains the vapor of the latter into the contact tube. The necessary ratio between the methyl chloride and the chlorosilane is maintained by regulating the temperature in the mixer. The contact process is effected in a glass tube 75 mm in diameter and 600 mm long, into which 500 g of aluminum* have been charged. The tube is heated by a muffle furnace. The products of the reaction pass from the contact apparatus into a trap for the aluminum chloride (in which the temperature is maintained at 100°C), after which they are routed to the condenser.

Zinc powder may be used instead of aluminum as the halogen acceptor. The following figures enable us to evaluate the effectiveness of the process.

When equimolecular quantities of methyltrichlorosilane and methyl chloride are passed over aluminum at 450°C, a condensate is formed, consisting of 21% of trimethylchlorosilane, 11% of dimethyldichlorosilane, and traces of methyldichlorosilane; at 350°C, 6.3% of trimethylchlorosilane and 4.5% of dimethyldichlorosilane are formed.

From equimolecular quantities of methyl chloride and dimethyldichlorosilane, when passed over aluminum at 350°C, 30% of trimethylchlorosilane is obtained. The same results is obtained if the mixture is passed over zinc at 375°C.

* The particles must be of such size that they will pass a No. 80 sieve.
By passing dimethyldichlorosilane and ethyl chloride over aluminum at 350°C, dimethylethylchlorosilane can be prepared; 2 mols of dimethyldibromosilane and 1 mol of methyl bromide, when passed over aluminum at 350°C, form trimethylbromosilane.

\( \text{SiCl}_4 \) under these conditions is also able to react with alkyl chlorides, but the process proceeds with extreme slowness and the yield of the process is so insignificant that the individual reaction products cannot be separated.

Alkylchlorosilanes containing the Si-H bond, may be similarly prepared, by passing a mixture of hydrogen and an alkylchlorosilane through a contact apparatus. Thus, an equimolecular mixture of methyltrichlorosilane and hydrogen at 450°C, when passed over aluminum, forms up to 5% of methyldichlorosilane:

\[
6\text{CH}_3\text{SiCl}_3 + 3\text{H}_2 + 2\text{Al} \rightarrow 6\text{CH}_3\text{SiHCl}_2 + 2\text{AlCl}_3
\]

Dimethyldichlorosilane does not react under these conditions. Yu.C.Mamedaliyev and others have proposed the preparation of alkylhalosilanes by the action of unsaturated hydrocarbons, ethylene and HCl on an alloy of iron, silicon, and 20% of copper, at 270-410°C. The authors believe that HCl adds to ethylene, forming ethyl chloride, which then, under the catalytic influence of the copper, reacts further with silicon to form ethylchlorosilanes (Bibl.60). A method of preparing the alloy, is described, and it is shown that with certain ratios of silicon to copper, an alloy is obtained which, when reacted with ethyl chloride, propyl chloride, or tert-butyl chloride, will yield mainly alkyltrichlorosilanes and dialkyldichlorosilanes. The reaction with tert-butyl chloride is also accompanied by side processes, the formation of resins and gaseous hydrocarbons (Bibl.61).

The alkylhalosilanes may also be prepared by the action of aluminum chloride, ferrous chloride, or bismuth trichloride on tetra-substituted silanes by the reaction (Bibl.62):

\[
3(\text{C}_2\text{H}_5)_2\text{Si} + 2\text{BiCl}_3 \rightarrow 5(\text{C}_2\text{H}_5)_2\text{SiCl} + 3\text{C}_2\text{H}_5\text{Cl} + 2\text{Bi}
\]
This reaction proceeds only at high temperature. The heating of the tetraethylsilane with bismuth trichloride in ether and alcohol up to their boiling points does not lead to the cleavage of the organic radical. However, heating tetraethylsilane with bismuth trichloride at the boiling point of tetraethylsilane for only 2 hours does lead to the formation of triethylchlorosilane.

**Method of Preparing Pure Trialkylchlorosilanes**

When 36% HCl acts on hexamethyldisiloxane, the cleavage of the siloxane bond takes place, and a certain amount of trimethylchlorosilane is formed:

\[
(CH_3)_3SiOSi(CH_3)_3 + 2HCl \rightarrow 2(CH_3)_3SiCl + H_2O
\]

This reaction is the only example of the cleavage of the siloxane bond under the action of HCl, and demonstrates the weakness of the bond between the trialkylsilyl group and other atoms or groups. This peculiarity of the trialkylsilyl group has been used for certain reactions for preparing trialkylchlorosilanes (Bibl.63).

Hexaalkyldisiloxanes readily react with concentrated sulfuric acid, forming a sulfate:

\[
R_3SiOSiR_3 + 2H_2SO_4 \rightarrow 2(R_3SiO)SO_3H + H_2O
\]

The sulfates so obtained react with HCl to form a trialkylchlorosilane:

\[
(R_3SiO)SO_3H + HCl \rightarrow R_3SiCl + H_2SO_4
\]

Only the trialkylsilyl group is distinguished by the ability of entering into a reaction of this type; bifunctional structural units R₂Si < do not react at all, so that only the trialkylchlorosilane is present in the product. The preparation of fluorotrialkylchlorosilanes by this method may be of practical interest.

**Preparation of Triethylchlorosilanes from Hexaethyldisiloxane.** To 275 ml of sulfuric acid of specific gravity 1.84, 265 g of hexaethyldisiloxane is added under
stirring, after which, 175 g (or a somewhat smaller amount) of ammonium chloride is added gradually, over a period of 2 hours, with stirring. The stirring is continued for another hour, then the upper layer is taken off and the reaction product is distilled from a flask provided with a column. The yield of triethylchlorosilane is 80-90% of theoretical, the purity of the product depending on the care with which the solvent was removed from the hexaethyldisiloxane. When rectified hexaethyldisiloxane is used, with the boiling point 230-235°C, the triethylchlorosilane may be obtained in the chemically pure state.

Chemically pure trimethylchlorosilane may be prepared similarly from hexamethyldisiloxane.

The preparation of trimethylchlorosilane from hexamethyldisiloxane is described on page 534.

Tripropyl- and tributylchlorosilanes may be prepared by the method described above for the preparation of triethylchlorosilane.

Another reaction which also leads to the formation of trialkylchlorosilanes (Chl. 50), is that between trialkylaminosilanes and HCl:

\[ R_3SiNH_2 + 2HCl \rightarrow R_3SiCl + NH_4Cl \]

Preparation of Triethylchlorosilane from Triethylaminosilane. 1. To 160 ml of concentrated HCl, 13 g of triethylaminosilane is added over a period of half an hour. The upper layer is removed, dried over anhydrous sodium sulfate, and distilled, yielding 12 g of triethylchlorosilane, or 80% of theoretical. Chloroethyldiethylchlorosilane is prepared similarly, from chloroethyldiethylaminosilane, in a yield 79% of theoretical.

A different method of conducting this reaction is also possible.

2. Through a solution of 20 g of triethylaminosilane in 150 ml of ether, hydrogen chloride is bubbled. On the completion of the reaction, the ammonium chloride is filtered off and the filtrate is distilled. The yield of triethylchlorosilane...
is 70% of theoretical. Chloroethyltriethylchlorosilane in 76% yield is prepared under similar conditions from chloroethyldiethylaminosilane.

The tetra-substituted silanes containing a halogen atom in the side chain are able to undergo rearrangement under the action of small amounts (1%) of ammonium chloride at 80-100°C, forming trialkylchlorosilanes, for example:

\[
\text{CH}_3\text{SiHCl}_2 \rightarrow \text{CH}_3\text{SiH}_2\text{Cl}
\]

The trialkylchlorosilanes are formed under the action of elementary chlorine, or of alkyl halides (in the presence of ammonium chloride) on trialkylsilanes containing the Si-H bond. Under the action of benzoyl chloride or phosphorus chlorides on substituted esters, or of phosphorus pentachloride on silanols (for example, on triphenylsilanol), alkyl- and arylchlorosilanes may also be prepared.

Alkylhalosilanes may be prepared by the action of alkylhalides on polyhalosilanes:

\[
\text{SiCl}_4 + \text{RCl} \rightarrow \text{RSiCl}_3 + \text{HCl}
\]

This reaction proceeds in the presence of the catalysts CuCl, SbCl₃, etc, at a temperature of 100-150°C (Bibl.6L).

**Preparation of Alkyl-(Aryl)-Fluorosilanes**

**Preparation of Alkyl-(Aryl)-Fluorosilanes by the Aid of Organomagnesium Compounds**

In contrast to SiCl₃, SiF₄ reacts so actively with organomagnesium compounds that it is impossible to control the process properly. The principal reaction product is a trialkyl- or triarylfluorosilane, and the tetraalkylsilane is also frequently formed. Dialkyldifluorosilanes can be prepared by this method only where the organic radical they contain is branched (for instance by the aid of isopropylmagnesium chloride).

The replacement of three atoms of fluorine proceeds very rapidly and so well
that a general method of adding three organic radicals to the silicon atom may be based on this reaction. Thus, for example, the synthesis of the trialkyliodosilanes, $R_3SiI$, and the tetra-substituted silanes $R_3SiR$, is most conveniently conducted by way of the trialkylfluorosilanes, prepared according to the reaction:

$$3RMgCl + SiCl_4 \rightarrow R_3SiCl + 3MgCl_2$$

followed by iodination or alkylation of the trialkylfluorosilanes.

The reaction for the preparation of the trialkylfluorosilanes from $SiCl_4$ and organomagnesium compounds was first investigated, in 1935, by Medoks and Kotelkov, on the example of triphenylfluorosilane (Bibl.65).

Preparation of Triphenylfluorosilane. $SiF_4$, (prepared by heating a mixture of 3.5 g of $CaF_2$, 6 g of glass powder, and 33 g of sulfuric acid) is passed for 2 hours 45 min through a tube with glass wool (to remove the HF) into a flask with a solution of phenylmagnesium bromide (prepared from 3.6 g of magnesium shavings, 24.9 g of bromobenzene, and 75 ml of ether). The product reacted completely. The trialkylfluorosilanes do not react with water, and therefore the precipitate of magnesium fluorobromide is washed away with water acidified by $HC\text{I}$ (50 ml). The product is extracted with 30 ml of ether, the extract is evaporated, and the triphenylfluorosilane is separated by rectification at the boiling point 200-210°C (10 mm).

Medoks (Bibl.65) similarly prepared tribenzylfluorosilane, in 6-7 g yield from 33.77 g of benzylchloride, 6.49 g of magnesium, 121 ml of ether, and $SiF_4$ vapor; boiling point 235.5°C (7.6 mm).

A number of trialkylfluorosilanes may be prepared by the same method (Bibl.66, 67). $SiF_4$ may be prepared, either by the above method, or by the action of sulfuric acid on a mixture of $NaF_4$ and silica. The product may be most simply purified by passing it through tablets of $NaF_4$, which absorb HF.

The reaction with ethylmagnesium bromide gives a relatively low yield, and tetraethylsilane is formed together with triethylfluorosilane.
The precipitate of magnesium salts may be washed away by a weak solution of sulfuric acid; the washed solution is dried and rectified, yielding 11% of triethylfluorosilane and 15% of tetraethylsilane.

Propyl-, butyl-, and amylmagnesium chloride react under similar conditions only to form trialkylfluorosilanes, and in considerably better yields; the yield of tri-propylfluorosilane is 43% of theoretical and that of triamylfluorosilane is 58%.

When SiF₄ is passed for 6 hours over a solution of isopropylmagnesium chloride in 500 ml of ether, reaction takes place, forming a mixture of diisopropyldifluorosilane, in 13.5% yield, and triisopropylfluorosilane, in 7.5% yield. The reaction mixture is likewise separated by washing, drying, and rectification.

The yield of triethylfluorosilane by the Grignard reaction was 15%, that of tri-propylfluorosilane, 62%, that of tributylfluorosilane, 70.1%, that of triamylfluorosilane, 57.6%. The fluorosilanes are very stable. The fluorine attached to a silicon atom cannot be split off even by reaction with sodium in liquid ammonia.

Preparation of Alkyl-(Aryl)-Fluorosilanes by Fluorination of Polyorganosiloxanes

The replacement of hydrogen atoms by fluorine atoms is effected by the action of HF on polyorganosiloxanes in the presence of water-removing agents (Ribl.68):

\[ \text{Si} - \text{C} + \text{HF} \rightarrow \text{Si} - \text{F} + \text{H}_2 \text{O} \]

The Si-C bond is completely stable against the action of HF, and therefore the process can be conducted with almost quantitative yield.

This reaction makes it possible to prepare most alkyl- and arylfluorosilanes by hydrolysis of the corresponding alkyl- or arylchlorosilanes and treatment of the hydrolysis products with HF or ammonium fluoride in the presence of sulfuric acid. For instance trimethylfluorosilane may be prepared from hexamethyldisiloxane and ammonium fluoride by the reaction:
Preparation of Alkylfluorosilanes from Polyalkyldisiloxanes. In a flask provided with a stirrer and a mercury seal, is placed a mixture of polymethylsiloxanes (prepared by hydrolysis of a mixture of methylchlorosilanes) with 80% oleum, and a small amount of a wetting agent (tergitol). Into the flask, with stirring, HF is bubbled, and the gaseous methylfluorosilanes formed are passed through tablets of sodium fluoride into a condenser, where they are condensed by means of solid carbon dioxide or liquid nitrogen. The mixture of methylfluorosilanes may be separated in a special low-temperature rectification column.

Trimethylfluorosilane may be prepared by a considerably simpler method.

To 196 g of concentrated sulfuric acid, 81 g of hexamethyldisiloxane is added with stirring and cooling with ice. Then 18.1 g of ammonium fluoride is gradually introduced into the reaction mixture, with stirring and slight warming. The trimethylfluorosilane is caught by means of ether.

Diethyl and ethylfluorosilanes are prepared similarly:

The product of the hydrolysis of diethyldiethoxysilane are mixed with sulfuric acid, and then, with stirring, ammonium fluoride (or calcium fluoride) is gradually added to the mixture. The mixture is allowed to stand, the upper layer is then separated, and the diethyldifluorosilane is separated from it by fractional distillation.

Ethyltrifluorosilane is prepared from the hydrolysis product of ethyltrichlorosilane, sulfuric acid, and calcium fluoride. Dimethyltrichlorosilane is prepared by the action of 50 g of ammonium chloride on a mixture of 62 g of tetramethyldisiloxanes and 100 ml of sulfuric acid at a temperature not higher than 15°C. The ammonium fluoride is introduced over a period of 1.5 minutes, after which the mixture is poured onto ice, washed, dried, and rectified; the yield of dimethyltrichlorosilane is 75%, and its boiling point is 19.8°C (742 mm).
fluorosilane is 60% yield, and a number of other alkylfluorosilanes, have been prepared by this method (Bibl.67).

Preparation of Alkyl-(Aryl)-Fluorosilanes by the Fluorination of Alkyl-(Aryl)-Chlorosilanes

The reaction is conducted by the action, on alkyl-(aryl)-chlorosilanes, of fluorinating agents: fluorides of tin, zinc, lead HF, and most often, the most active reagent of all, antimony trifluoride, which is usually used in the presence of antimony pentachloride. The principal product of the reaction is a compound in which the chlorine has been completely replaced by fluorine, since the initial temperature at which the replacement of the first chlorine atom, takes place, as a rule, is higher than the temperature of replacement of the following chlorine atoms.

It is also possible to separate intermediate reaction products, whose yield is increased when larger amounts of antimony pentachloride are used.

Fluorination of Alkylchlorosilanes (Bibl.67, 68, 69). In a glass flask, provided with a stirrer, and which serves as the retort for a rectification column, the alkylchlorosilanes and fluorinating agents are placed. The reaction is conducted under reduced pressure in order completely to remove the fluorides formed in the form of gases. The reaction products, after passing through the rectification column, where the unreacted alkylchlorosilanes are separated and returned to the still for the fluorination, are condensed by cooling with solid carbon dioxide or liquid nitrogen.

1. Fluorination of methyltrichlorosilane proceeds well under the action of antimony trifluoride in the presence of antimony pentachloride at 150°C. The reaction product is methyltrifluorosilane with a small admixture of methyldifluorosilane. If the fluorination is conducted by passing methyltrichlorosilane vapor over calcium fluoride at 200°C, all three products of fluorination are formed in equivalent amounts, but in insignificant yield.

2. The fluorination of dimethyldichlorosilanes by antimony trifluoride in the
presence of antimony pentachloride yields dimethyldifluorosilane mixed with an insignificant amount of dimethylfluorochlorosilane.

As we have stated, methyldichlorosilane is very difficult to separate from traces of dimethyldichlorosilane. The separation of these products may be effected by fluorination of the mixture under residual pressure of 50 mm. In this case the dimethyltrichlorosilane is completely fluorinated, while the methyltrichlorosilane remains unchanged.

3. The fluorination of trimethylchlorosilane may be conducted either with the pure starting material or in a mixture with SiCl\(_4\) (51-57°C fraction), since SiCl\(_4\) is not fluorinated by antimony trifluoride or by zinc fluoride. The fluorination of the methylchlorosilane may be accomplished by the action of zinc fluoride dried 24 hours at 100°C. The mixture is heated at the boiling point, and the fluorides formed are removed through the rectification column and condensed on cooling with solid carbon dioxide.

4. The fluorination of methyldichlorosilane may be accomplished by the action of a mixture of antimony trifluoride and antimony pentachloride at room temperature; in this case, together with methyldifluorosilane in 35% yield, a considerable amount of methylfluorochlorosilane (in 15% yield), an intermediate fluorination product, is also formed.

5. The fluorination of methyldichlorosilane by the aid of antimony trifluoride (in the absence of antimony pentachloride) (Bibl.69) proceeds at a temperature of about 20°C, under atmospheric pressure. The average yield of the fluorination products was about 50%, and they consisted of about 70% of methyldifluorosilane and 30% of methylfluorochlorosilane. Thus the Si-H bond is preserved on fluorination. The fluorination products were condensed in a bulb cooled by liquid nitrogen, and were then fractionated on a low-temperature column. A solution of solid carbon dioxide and acetone was used as the cooling agent during rectification.

6. Fluorination of ethyltrichlorosilane (215 g) by the action of antimony
trifluoride in the presence of antimony pentachloride at 40°C under residual pressure of 225 mm leads to the production of a mixture consisting of 70 g of ethyltrifluorosilane, 8 g of ethyldichlorofluorosilane, and 15 g of ethylchlorodifluorosilane.

7. On fluorination of propyltrichlorosilane by antimony trifluoride in the presence of antimony pentachloride under a pressure of 460-480 mm, propyltrifluorosilane is formed in 80% yield; at a residual pressure of 200 mm, traces of the intermediate fluorination products are also formed. The products are separated by rectification at 500 mm; propyltrifluorosilane in vacuo boils at 15-16°C, propylchlorodifluorosilane at 55-57°C, and propyldichlorofluorosilanes at 88-90°C. The yield of intermediate products of fluorination is increased when a diluent (tetrachloroethylene) is used.

It has been noted that propyltrifluorosilane, like an aryltrifluorosilane, is usually converted into a glass like mass on freezing (crystals are obtained with great difficulty).

8. Fluorination of isopropyltrichlorosilane by antimony trifluoride at 20°C and a residual pressure of 100-300 mm, leads to the formation of 70-75% of isopropyltrifluorosilane, 8-10% of isopropylidifluorochlorosilane, and 17-20% of isopropylfluorodichlorosilane.

9. Fluorination of butyltrichlorosilane by antimony trifluoride in the presence of antimony pentachloride at 70-125°C and a residual pressure of 175-425 mm, yields 33-40% of butyltrifluorosilane, 1-4% of butyldifluorochlorosilane, and 5-10% of butylfluorodichlorosilane.

The low yields of the intermediate fluorination products are noted. The authors explain this by the fact that the replacement of each chlorine atom by a fluorine atom takes place at a definite temperature, below which this reaction does not proceed. This temperature decreases with the increasing number of fluorine atoms in the molecule. Thus, if the reaction temperature is higher, for instance, then the temperature of formation of propyldichlorofluorosilane, then the process of
fluorination will continue.

**Preparation of Phenylfluorosilanes by the Fluorination of Phenylchlorosilanes.**

1. A mixture consisting of 4.6 mol of phenyltrichlorosilane, 2.4 mols of antimony trifluoride, and 1 ml of antimony pentachloride is heated 6.5 hours at 60-80°C and residual pressure 6-7 mm, yielding 1.75 mols of phenyltrifluorosilane, 0.44 mol of phenyl trifluorochlorosilane, and 0.41 mol of phenylfluorodichlorosilane.

2. On heating 2.53 mols of diphenylchlorosilane and 4.03 mols of lead tetrafluoride at 145-160°C (7 mm), a mixture of diphenyltrifluorosilane and diphenyl- fluorochlorosilane is formed.

Under the action of zinc fluoride on the corresponding organochlorosilanes, the following compounds were prepared: ethyltrifluorosilane, phenyltrifluorosilane, dimethylchlorosilane, diethylfluorosilane, diphenylfluorosilane, triethylfluorosilane, and triphenylfluorosilane (Bibl.70, 71, 72).

Fluorination may also be accomplished under the action of dry HF. Dibutylchlorosilane reacts with HF at 0°C, and on subsequent slow warming of the mixture to room temperature over a period of 10 hours. The excess of HF is precipitated by sodium fluoride, and the reaction product is then filtered and rectified. The yield of dibutylfluorosilane is 70%. Mono-, di-, and triallylfluorosilanes, as well as phenylfluorosilanes, may be similarly prepared.

The action of HF on compounds of the type $R_xSiCl_{4-x}$ takes place rapidly, even without the use of catalysts. The formation of neither hydrocarbons nor tetrafluorosilane was observed. Anhydrous HF was placed in a copper boiler cooled with ice, and the alkylchlorosilane was added to it. The reaction mixture was then warmed to room temperature over a period of 8-10 hours, the excess of HF was removed by NaF, and the precipitate was washed away with benzene. In this way the following compounds were prepared: $(C_6H_5)_2SiF_2, C_7H_{11}SiF_3, (C_5H_{11})_2SiF_2, (C_5H_{11})_3SiF, C_4H_9SiF_3, (C_4H_9)_3SiF, CH_3SiF_3, (CH_3)_2SiF_2, (C_4H_9)_2SiF_2$.

The activity of these compounds varied with the number of fluorine atoms in the
molecule (Bibl.73, 74, 75, 76, 77).

These products are insoluble in water, and their hydrolysis proceeds on the phase separation interface. The products are soluble in petroleum ether, benzene, toluene, chlorinated hydrocarbons, ether and ethyl acetate. They are soluble in acetone, but apparently enter into reaction with it, since the solution on standing first takes on a pale yellow color, which passes on further standing into a dark red. It is possible that under the action of butylfluorochlorosilanes, acetone is dehydrated, and mesityl oxide, or phorone, is formed from it. This reaction has not been investigated.

On the reaction with alcohols, each of the halides behaves differently, according to the nature of the halide and the alcohol. With methyl alcohol, for instance, all three halides react, trifluorosilane, dichlorofluorosilane, and difluorochlorosilane. In butanol, on the contrary, butyltrifluorosilane is esterified very slowly. Iron, steel, copper, and platinum do not react with butyltrifluorosilane and mixed butylfluorochlorosilanes at ordinary temperatures. Butyltrifluorosilane is toxic, and the inhalation of small amounts of it causes violent headache and a dazed condition. The mixed halides do not possess this property, but they are still lacrimators.

Preparation of Alkyl-(Aryl)-Fluorosilanes by Fluorination of Alkoxy-and Aminosilanes

Alkyl-(aryl)-fluorosilanes are also prepared by fluorination of organosilicon compounds containing the Si-O, Si-Cl or Si-N bond, by means of HF.

The synthesis of organofluorosilanes from organoalkoxysilanes and organochlorosilanes by the action of an aqueous solution of HF at 0°C has been described.

We present a typical example of the synthesis of a dialkyldifluorosilane.

Preparation of Dipropyldifluorosilane by Fluorination of Dipropyldiethoxysilane (Bibl.186). In a 1250 cm³ flask provided with a stirrer, and cooled in an ice bath at 0°C, 100 g (2.4 mols) of 48% HF and 52 g (0.258 mols) of dipropyldiethoxysilane are placed. The mixture is stirred 3 hours and then the upper organic layer is
removed. Fractionation of the organic layer yields 37.0 g (0.243 mol) of dipropyl-
difluorosilane, in 97.5% yield.

Alkyl-(aryl)-fluorosilanes are formed by the action of HF on aminosilanes
(Bibl.50). The aminosilanes are prepared by the action of ammonia on alkylchloro-
silanes. The reaction with trialkylaminosilanes proceeds most easily.

Preparation of Triethyfluorosilanes by Fluorination of Triethylaminosilane. To
60 mol of HF, cooled by ice, 12 g of triethylaminosilane are added over a period of
5 min. After standing for 10 minutes, the upper layer is removed, dried over sodium
sulfate, and distilled, yielding 89% of triethylfluorosilane. Chloroethyldiethyl-
fluorosilane in 82% yield can be similarly prepared from chloroethyldiethylamino-
silane.

Preparation of Alkyl-( Aryl)-Bromosilanes

The synthesis of alkyl-(aryl)-bromosilanes by means of organometallic compounds
from the corresponding tetrahalosilanes has not been described in the literature and
is not of practical interest. They are prepared by the reaction of alkyl bromides
with a copper-silicon contact mass, under the action of HBr on alkylaminosilanes, or
by the reaction of tetrabromosilane with diazomethane.

When an alkyl bromide or aryl bromide reacts with a copper-silicon contact mass
(Bibl.28), a mixture of the corresponding alkyl-(aryl)-bromosilanes is formed.

From the products of the reaction between methyl bromide and a 20% copper-
silicon contact mass at 275°C, trimethylbromosilane and methyltribromosilane can be
separated by rectification. The main products of the reaction at a temperature up
to 280°C is probably dimethylidibromosilane, since on the hydrolysis of the mixture
obtained on the reaction, a liquid polymethylsiloxane, coagulating only after heat-
ing for a day at 200°C, is formed.

Bromobenzene reacts with an oxidized 50% copper-silicon alloy at 430°C to form
diphenylidibromosilane.
In recent years, A.V. Topchiyev and his associates have conducted studies on the synthesis of various alkyl-(aryl)-halosilanes. Under the action of methyl bromide on metallic silicon in the presence of copper at 385°C, dimethyldibromosilane, methyltribromosilane, and traces of trimethylbromosilane have been obtained (Bibl.78).

The reaction of bromobenzene and silicon proceeds readily in the presence of copper; at 410°C, phenyltribromosilane, diphenyldibromosilane, and triphenylbromosilane are formed (Bibl.136).

A convenient method of preparing alkylbromosilanes is based on the reactions between HBr and aminosilanes (Bibl.66).

\[
(C_3H_5)_4Si + 2HBr \rightarrow (C_3H_5)_3SiBr + H_2
\]

The aminosilanes are prepared by treating alkylchlorosilanes with ammonia.

**Preparation of Triethylbromosilane from Triethylaminosilane.** When dry HBr is passed to saturation through a solution of triethylaminosilane in 4 parts by volume of ether, triethylbromosilane is obtained in yield 70% of theoretical. Chloroethyl-diethylbromosilane may be prepared under similar conditions. The yield of the product is 20%.

A purer product is obtained by the following method. To 300 mm of 48% HBr, under ice cooling, 200 ml of concentrated sulfuric acid is added, followed by 41 g of triethylaminosilane. After standing for 20 minutes under stirring, the organic (upper) layer is removed and dried; and the triethylbromosilane is distilled under reduced pressure; boiling point 78-79°C (45 mm). The yield is 33.5 g, or 55%.

Chloroethyl-diethylbromosilane is prepared under similar conditions in yield of 81%.

A general method of preparing di- and trialkyl-(aryl)-bromosilanes is the replacement of the phenyl group in tetra-substituted silanes by bromine, under the action of elementary bromine:

\[
R_2Si + C_4H_4Br_2 \rightarrow R_2SiBr + C_4H_4Br
\]
When a mixture of tetraphenylsilane (Bibl.79) and bromine is heated 8-10 hours at 150°C in a sealed tube, triphenylbromosilane, diphenyldibromosilane, and bromobenzene are formed. Trimethylbromosilane may be prepared by heating an equimolecular mixture of trimethylphenylsilane and bromine on a water bath for 1 hour.

Bromoalkylbromosilanes containing a bromine atom in the α-position, may be prepared by the reaction of tetrabromosilane with diazo compounds (Bibl.58). The reaction proceeds better than with SiCl₄, and the principal products formed are di- and trialkylbromosilanes:

\[
\begin{align*}
\text{SiBr}_4 + 2\text{CH}_3\text{N}_2 & \rightarrow (\text{CH}_3\text{Br})_3\text{SiBr} + 2\text{N}_2 \\
\text{SiBr}_4 + 3\text{CH}_3\text{N}_2 & \rightarrow (\text{CH}_3\text{Br})_3\text{SiBr} + 3\text{N}_2
\end{align*}
\]

Preparation of Alkyl-(Aryl)-Iodosilanes (Bibl.57)

The synthesis of alkyliodosilanes may be accomplished either by cleavage of the organic radical from tetra-substituted silanes under the action of iodine in the presence of aluminum iodides, or by the action of aluminum triiodide on an alkylchlorosilane or alkylsilane containing the Si-H bond.

The cleavage of the phenyl radical is easiest under the action of iodine:

\[
(\text{C}_6\text{H}_5)\text{Si}(\text{CH}_3)_3 + \text{I}_2 \rightarrow (\text{CH}_3)\text{SiI} + \text{C}_6\text{H}_5\text{I}
\]

Even in the absence of a catalyst, the reaction proceeds on heating of the mixture by 2 hours (yield 55%).

The use of aluminum iodide (or of aluminum that subsequently reacts with iodine) sharply accelerates the process of cleavage of the Si-C bond by elementary iodine. Thus, for example, the above reaction with trimethylphenylsilane takes place quantitatively in 20 min. Aluminum iodide does not react in the absence of iodine, even on prolonged boiling.

The rate of cleavage of the aliphatic radicals is considerably slower than that of the phenyl radical. The cleavage of methyl is easier than that of the others,
that of ethyl goes about twice as slowly, and that of propyl and isopropyl still more slowly.

Preparation of Alkylidodasilanes by Iodination of Alkylsilanes. In a flask are placed 14.4 g of tetraethylsilane and 0.2 g of aluminum powder, and a stream of dry nitrogen is passed through it. The mixture is heated to the boiling point, after which 25.4 g of iodine is added gradually over a period of 1.5 hours, and the ethyl iodide formed during the reaction is distilled off. The reaction product is rectified, yielding 65% of pure triethylidodasilane, boiling point 190.5°C (744 mm). The yield of the unpurified product is 90%. To prepare diethyldiiododasilane, the charge of iodine is increased to 50.8 g and the time of heating to 9 hours. The yield of unpurified product is 70%.

When 42 g of triethylidodasilane reacts with 22 g of iodine and 1.5 g of aluminum iodide for 2.5 hours, 40 g of diethylidodasilane, in 71% yield, is formed. A certain amount of butane is formed in all reactions.

When dimethyldiethylsilane reacts with iodine in the presence of aluminum iodide methyldiethyliodosilane and dimethyliodosilane are formed:

\[
\text{(CH}_3\text{)}_2\text{Si}(\text{C}_2\text{H}_5)_2 + J_2 \xrightarrow{\text{Al}} \text{CH}_3\text{J} + \text{CH}_3\text{Si}(\text{C}_2\text{H}_5)_2
\]

\[
\text{(CH}_3\text{)}_2\text{Si}(\text{C}_2\text{H}_5)_2 + J_2 \xrightarrow{\text{Al}} \text{CH}_3\text{J} + \text{(CH}_3\text{)}_2\text{Si}(\text{C}_2\text{H}_5)_2
\]

the number of mols of methyl iodide formed being twice the number of mols of ethyl iodide. When methyltriethylsilane reacts with iodine, this ratio amounts to 2 : 3; thus, taking account of the ratio between the number of radicals in the original compounds, it must be recognized that the rate of cleavage of the methyl radicals is twice the rate of cleavage of ethyl radicals. On the cleavage of dimethylisopropylsilane, the ratio between the number of mols of methyl iodide and propyl iodide is 4 : 1, and, on the cleavage of n-propyldimethylsilane, is 2 : 1. When phenyltrimethylsilane reacts with iodine, only iodobenzene and trimethyliodosilane are formed.

In some cases, the reaction products are rather hard to separate by rectifica-
tion. To investigate its composition, it is most convenient to fluorinate the mixture, and then to rectify the alkylfluorosilanes formed. Sometimes it is more convenient to hydrolyze the product and then to fluorinate the siloxane so formed by the action of HF in the presence of sulfuric acid.

The iodination of the alkylfluorosilanes may be accomplished either by the action of iodine in the presence of aluminum iodide at the boiling point of the mixture, or by the action of aluminum iodide alone:

$$3R_3SiF + AlI_3 \rightarrow 3R_3SiJ + AlF_3$$

**Preparation of Alkylidiosilanes by Iodination of Alkylfluorosilanes.** On heating 14 g of triethylfluorosilane and 0.4 g of aluminum with 13 g of iodine, 18 g of triethyliodosilane is formed. Boiling point 190-191°C. On 1.5 hours heating of 10 g of tripropylfluorosilane with 7 g of iodine, 7.5 g of tripropyliodosilane, boiling point 235°C, is similarly obtained.

On adding 10 g of triethylfluorosilane to 9.5 g of aluminum, the mixture heats up strongly. After the mixture is heated for 1 hour, its rectification may yield 10 g (56%) of triethyliodosilane (the yield of the unpurified product is almost the theoretical). Tripropyliodosilane is 70% yield, methyldipropyliodosilane in 25% yield, and diethylpropyldiiodosilane in 33% yield are similarly prepared.

Lithium iodide does not react with triethylfluorosilane. Under the action of iodine on triethyldisilane, the hydrogen is easily replaced by iodine:

$$\left(C_3H_6\right)SiH + J_2 \rightarrow HJ + \left(C_3H_6\right)SiJ$$

After heating 23 g of triethyldisilane and 48 g of iodine for half an hour, the excess of iodine is removed by adding magnesium shavings. The yield of triethyliodosilane is 85% of theoretical.

The synthesis of alkylidiosilanes is also accomplished by the reaction:

F-TS-9191/V 461
Dimethylidiodosilane, methyltriiodosilane, propyltriiodosilane, butyltriodosilane and amyltriiodosilane have been prepared by this method (Bibl. 208).

By heating equimolecular quantities of a mixture of methyltrichlorosilane and methyltriodosilane 20 hours at 300°C, methyldichloroiodosilane, methylchlorodiodosilane and dimethylechloroiodosilane were obtained. Heating diethyldichlorosilane with diethyldiodosilane for 10 hours at 400°C yielded diethylchloroiodosilane.

In metathesis (without the use of catalysts), the alkyl groups are not exchanged but in the presence of aluminum trichloride the replacement of alkyl groups by halogens does take place (Bibl. 87).

Physical Properties of Alkyl-(Aryl)-Halosilane.

The overwhelming majority of alkyl-(aryl)-halosilanes are colorless liquids with a sharp odor. Only isolated representatives, mainly the higher trialkyl and triarylhalosilanes are solid crystalline substances under ordinary conditions.

The sharp odor of alkylhalosilanes is due to the liberation of hydrogen halide owing to the hydrolytic processes that take place on contact with the moisture of the air. In compounds which are distinguished by hydrolytic stability (for instance in trialkylfluorosilanes), the odor of hydrogen halides is considerably fainter, or even disappears entirely, and thus it is possible to distinguish the faint and usually ethereal odor of the compound itself. Even when the hydrolysis of the products proceeds readily, the intrinsic odor of the alkylhalosilanes is mixed with the odor of hydrogen halide. Sometimes this odor is sharp, thus, for instance, the methylchlorosilanes have the sharpest and most unpleasant odor, which is even sharper than that of SiCl₄.

The methylfluorosilanes do not fume in moist air, but they still hydrolyze.
rapidly, and therefore possess the odor of HF.

The mixed fluorosilanes have an unpleasant odor.

The density of the alkyl-(aryl)-halosilanes is usually somewhat higher than unity, but it varies sharply according to the kind and number of the halogen atoms, and also according to the molecular weight of the organic radical: with increasing percentage of the organic part of the molecule (with increasing molecular weight and increasing number of organic radicals), the density decreases, sometimes going down to 0.9. The arylhalosilanes are usually distinguished by a considerably higher density than the alkylhalosilanes, which is evidence of the compactness of their molecular structure. The bromosilanes and iodosilanes have a considerably higher density than chlorosilanes (going up to 2, and even higher in isolated cases).

The density is one of the most important indexes for evaluating the purity of an alkylhalosilane. Thus, for instance, one of the methods of checking, in the separation of methyltrichlorosilane from dimethyltrichlorosilane by rectification, may be the determination of the density of intermediate fractions. From the value of the density the composition of the binary mixture can be rather precisely established since the density of the chlorosilanes differs substantially (1.2691 for methyltrichlorosilane and 1.0663 for dimethyldichlorosilane at 25°C), and the density of mixtures is an additive quantity (Bibl.68).

The boiling point of alkyl-(aryl)-halosilanes varies within very wide limits, and, like the hydrocarbons, may be calculated by the following empirical formula (Bibl.53):

\[ t_{bp} = 230.14 + \frac{N}{543} \]

where \( N \) represents the sum of values selected by calculation for each atom or organic radical included in the composition of the molecule of alkyl-(aryl)-halosilane.

Table 53 gives a number of such values (the so-called "boiling point numbers"), by which the boiling points of the lower organochlorosilanes can be roughly calculated.
Such compounds may have any combination of the lower radicals (CH$_3$, C$_2$H$_5$, C$_3$H$_7$, and C$_6$H$_5$), and also of alkyl-(aryl)-halosilanes containing the Si-H bond, of tetra-substituted silanes and of halosilanes.

The upper part of Table 53 gives the "boiling point numbers" for chlorine and bromine (from left to right in tri-, di-, and monoalkylhalosilanes, and in tetrahalosilanes; the last column gives the boiling point numbers for the trialkylhalosilanes that do not contain hydrogen atoms attached to the silicon. The lower part of Table 53 gives the "boiling point numbers" for the radicals of the mono-, di-, tri-, and tetra-substituted silanes.

Table 53

<table>
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<tr>
<th>Atom and Group Indices of the Boiling Point of Organosilicon Compounds</th>
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<tr>
<td>The Boiling Point Numbers of Si = 4.20; H = 0.60</td>
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<td>(X = Cl, Br; R = CH$_3$, C$_2$H$_5$, C$_3$H$_7$, and C$_6$H$_5$)</td>
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<tr>
<td>C$_6$H$_5$</td>
<td>18.87</td>
<td>18.76</td>
<td>18.41</td>
<td>17.73</td>
<td></td>
</tr>
</tbody>
</table>

We now present an example of the determination of a boiling point by the aid of the Table. Let us assume that we need to find the boiling point of methylchlorosilane, CH$_3$SiH$_2$Cl. For silicon the boiling point number is 4.20, for hydrogen 0.60, for chlorine in compounds of the type $\geq$SiCl, 5.05, for the methyl radical in $\geq$SiCH$_3$, 3.43. The sum of the boiling point numbers is 13.88.
According to the literature data, methylchlorosilane boils at 80°C.

As a rule the deviation of the values of the boiling point from the calculated value do not exceed 2%, but in occasional cases they reach 4-5°C. Thus this formula allows the boiling point to be roughly calculated for certain alkyl and arylchlorosilanes that are not described in the literature.

For all alkyl-(aryl)-chlorosilanes, the boiling points increase with the number of radicals bound to the silicon atom. The methylchlorosilanes are an exception: methyltrichlorosilane boils at 66.1°C, dimethyldichlorosilane at 70.1°C, trimethylchlorosilane at 54.6°C, and tetramethylsilane at 28°C.

Most alkyl-(aryl)-chlorosilanes and fluorosilanes distill without decomposition under atmospheric pressure, even under the conditions of prolonged rectification (tens of hours). It is advisable to distill the bromosilanes, and more particularly the iodosilanes, under reduced pressure, since they have considerably less thermal stability.

The melting point of the lower alkyl and arylchlorosilanes, as a rule, range from -50°C to -100°C.

The alkyl and arylchlorosilanes are readily soluble in organic solvents: aromatic hydrocarbons, halogen derivatives, ethers, etc (Bibl.81, 82).

There are statements that about 0.3% of the trimethylchlorosilane in a cyclohexane solution is in the form of the dimer (Bibl.83). Dimethyldichlorosilane forms a very unstable addition compound with ethyl ether (the maximum of the curve showing the relation between the variation of the dipole moment and the concentration corresponds to a 4-5% dimethyldichlorosilane content). The other methylchlorosilanes form no complexes with ethyl ether.

The measurement of the electron scattering of the vapors, and the spectra of the combination scattering of the methylchlorosilanes (Bibl.84) shows that the Si-Cl
The Si-C distance for dimethyldichlorosilane is 1.83 Å, for methyltrichlorosilane 1.94 Å, for trimethylchlorosilane 1.89 Å, for tetramethylsilane 1.93 Å, and for hexamethyldisilane 1.90 Å. The Cl-Si-Cl angle in dimethyldichlorosilane is 109.5°. The CH₃-Si-Cl angle in trimethylchlorosilane is from 106 to 112°.

The quantities of the methylchlorosilanes that form inflammable mixtures with air has been established (Bibl.85). Methyltrichlorosilane has the following limits of inflammability: lower, 7.6% of volume; upper, 20% by volume; dimethyldichlorosilane, 3.4% and 20% respectively; trimethylchlorosilane, 2.0% and 6.2% and methyl dichlorosilane, 3.4% and 34.0%.

Certain physical and chemical properties of propyldichlorofluorosilanes, propylchlorodifluorosilane, and propyltrifluorosilane has been investigated. The vapor pressure curve of these compounds obeys the Arrhenius equation: the logarithm of the vapor pressure (in millimeters) is proportional to a quantity that is the reciprocal of the absolute temperature plus the logarithm of the absolute temperature.

All the alkylfluorosilanes are colorless liquids with a pungent, irritant odor. Propyltrifluorosilane has a lacrimary action. These compounds do not fume in the air, and they do not dissolve in water; they are slowly hydrolysed by it, forming a gelatinous precipitate. Under the action of aqueous solutions of caustic alkali on them, hydrolysis proceeds considerably faster; as a result of hydrolysis water soluble products are formed. The products are soluble in ether and tetrachloroethylene. They do not react at the boiling point with nichrome and mercury. Glass wetted by an alkyltrifluorosilane becomes water-repellant. Water in tubes treated with propyltrifluorosilane has a horizontal meniscus. Table 54 gives the physical properties of the most important representatives of the organotrichlorosilanes. Table 55 gives
the properties of the dialkyl-(aryl)-dichlorosilanes and the trialkyl-(aryl)-chlorosilanes.

Table 56 gives the principal properties of the alkyl-(aryl)-bromosilanes and the alkyl-(aryl)-iodosilanes.

Table 57 gives the properties of the alkyl-(aryl)-fluorosilanes, and Table 58 the properties of the alkyl-(aryl)-fluorochlorosilanes.

Table 59 gives the properties of the alkylhalosilanes containing the Si-H bond. The values of the dipole moments of certain alkyl- and arylhalosilane has been determined, it has been shown that in absolute values, the quantities are close to the organic compounds of similar structure (Bibl.86) (cf. Table 60).

Table 61 gives the boiling points of azeotropic mixtures of chlorosilanes with other organic and organosilicon compounds.

Table 62 gives certain additional information on the properties of the methyl- and ethylchlorosilanes.
<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Density</th>
<th>Refractive index</th>
<th>Bibliography</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyltrichlorosilane</td>
<td>CH₃SiCl₃</td>
<td>0.948</td>
<td>1.4510</td>
<td>18</td>
</tr>
<tr>
<td>Ethyltrichlorosilane</td>
<td>C₂H₅SiCl₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vinyltrichlorosilane</td>
<td>C₃H₇SiCl₃</td>
<td>0.951</td>
<td>1.4503</td>
<td>52</td>
</tr>
<tr>
<td>Propyltrichlorosilane</td>
<td>CH₃CH₂SiCl₃</td>
<td>0.951</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allyltrimethylsilane</td>
<td>(CH₃)₃SiCl</td>
<td>0.948</td>
<td>1.4510</td>
<td>18</td>
</tr>
<tr>
<td>Butyltrichlorosilane</td>
<td>C₄H₉SiCl₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isobutyltrimethylsilane</td>
<td>(CH₃)₂CH₂SiCl₂</td>
<td>0.948</td>
<td>1.4510</td>
<td>18</td>
</tr>
<tr>
<td>Isopropyltrimethylsilane</td>
<td>(CH₃)₂CHSiCl₂</td>
<td>0.948</td>
<td>1.4510</td>
<td>18</td>
</tr>
<tr>
<td>tert-Isobutyltrimethylsilane</td>
<td>(CH₃)₂CH₂CH₂SiCl₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,3-Tetramethybutyltrimethylsilane</td>
<td>(CH₃)₂CH(C₂H₅)₂SiCl₄</td>
<td>0.948</td>
<td>1.4510</td>
<td>18</td>
</tr>
<tr>
<td>2,4,4-Trimethylpentyltrimethylsilane</td>
<td>(CH₃)₂CC(C₂H₅)₂CH₂SiCl₄</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Decyltrimethylsilane</td>
<td>C₁₀H₂₁SiCl₃</td>
<td>0.948</td>
<td>1.4510</td>
<td>18</td>
</tr>
<tr>
<td>Dodecyltrimethylsilane</td>
<td>C₁₂H₂₅SiCl₃</td>
<td>0.948</td>
<td>1.4510</td>
<td>18</td>
</tr>
<tr>
<td>Tridecyltrimethylsilane</td>
<td>C₁₃H₂₇SiCl₃</td>
<td>0.948</td>
<td>1.4510</td>
<td>18</td>
</tr>
<tr>
<td>Tetradecyltrimethylsilane</td>
<td>C₁₄H₃₃SiCl₃</td>
<td>0.948</td>
<td>1.4510</td>
<td>18</td>
</tr>
<tr>
<td>Hexadecyltrimethylsilane</td>
<td>C₁₆H₃₇SiCl₃</td>
<td>0.948</td>
<td>1.4510</td>
<td>18</td>
</tr>
<tr>
<td>Octadecyltrimethylsilane</td>
<td>C₁₈H₄₉SiCl₃</td>
<td>0.948</td>
<td>1.4510</td>
<td>18</td>
</tr>
<tr>
<td>Nonylphenyltrimethylsilane</td>
<td>C₁₀H₂₁SiCl₃</td>
<td>0.948</td>
<td>1.4510</td>
<td>18</td>
</tr>
<tr>
<td>p-Tolyltrimethylsilane</td>
<td>C₁₄H₁₆SiCl₃</td>
<td>0.948</td>
<td>1.4510</td>
<td>18</td>
</tr>
<tr>
<td>p-4-Ethoxyphenyltrimethylsilane</td>
<td>C₁₃H₂₇O₂SiCl₃</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 54: Physical Properties of Alkyl-(Aryl)-Trichlorosilanes**

- **a)** Name; **b)** Formula; **c)** Boiling point, °C; **d)** Specific gravity; **e)** Refractive index; **f)** Bibliography
<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>d) °C</th>
<th>c) d_20</th>
<th>e) n_20</th>
<th>f)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>p-Ethoxyphenyltrichlorosilane</strong></td>
<td>C_2H_5OCH_2SiCl_3</td>
<td>137-138</td>
<td>1.3660</td>
<td>-</td>
<td>21.22</td>
</tr>
<tr>
<td><strong>Benzyltrichlorosilane</strong></td>
<td>C_6H_5CH_2SiCl_3</td>
<td>216</td>
<td>1.2834</td>
<td>-</td>
<td>49.89</td>
</tr>
<tr>
<td><strong>α-Chlorobenzyltrichlorosilane</strong></td>
<td>C_6H_5CH(2)SiCl_3</td>
<td>162</td>
<td>-</td>
<td>-</td>
<td>49.89</td>
</tr>
<tr>
<td><strong>Cyclohexyltrichlorosilane</strong></td>
<td>C_6H_5H_3SiCl_3</td>
<td>208</td>
<td>-</td>
<td>1.3760</td>
<td>21.22</td>
</tr>
<tr>
<td><strong>α-Naphthyltrichlorosilane</strong></td>
<td>C_6H_5H_3SiCl_3</td>
<td>165-170</td>
<td>-</td>
<td>-</td>
<td>195</td>
</tr>
</tbody>
</table>

Table 55

Physical Properties of Dialkyl-((Diaryl)-Dichlorosilane and Trialkyl-(triaryl)-Chlorosilanes

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>d) °C</th>
<th>c) d_20</th>
<th>e) n_20</th>
<th>f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl dichlorosilane</td>
<td>(CH_3)2SiCl_2</td>
<td>70.1</td>
<td>1.06637</td>
<td>1.4002</td>
<td>6.29, 115</td>
</tr>
<tr>
<td>Dimethyl dichlorosilane</td>
<td>(CH_3)2SiCl_2</td>
<td>120</td>
<td>1.0504</td>
<td>1.4009</td>
<td>26.198</td>
</tr>
<tr>
<td>Diethyl dichlorosilane</td>
<td>(CH_3)2CHSiCl_3</td>
<td>118-119</td>
<td>1.086</td>
<td>-</td>
<td>39</td>
</tr>
<tr>
<td>Divinyl dichlorosilane</td>
<td>(CH_3)2CH=CHSiCl_3</td>
<td>184 (83 mm)</td>
<td>1.035</td>
<td>-</td>
<td>90</td>
</tr>
<tr>
<td>Diallyl dichlorosilane</td>
<td>(CH_3)2CH=CHSiCl_3</td>
<td>175, 176</td>
<td>195</td>
<td>-</td>
<td>195</td>
</tr>
<tr>
<td>Dipropyl dichlorosilane</td>
<td>(CH_3)2CHCHSiCl_3</td>
<td>67-69</td>
<td>1.06</td>
<td>-</td>
<td>20.21</td>
</tr>
<tr>
<td>Diisopropyl dichlorosilane</td>
<td>(CH_3)2CHCHSiCl_3</td>
<td>19</td>
<td>1.00</td>
<td>-</td>
<td>20.21</td>
</tr>
<tr>
<td>Diisobutyl dichlorosilane</td>
<td>(CH_3)2CHCHSiCl_3</td>
<td>160 (11 mm)</td>
<td>170</td>
<td>1.1790</td>
<td>1.4037</td>
</tr>
<tr>
<td>Heterocyclopentamethylendichlorosilane</td>
<td>(CH_3)2SiCl_2</td>
<td>302-305</td>
<td>223-225</td>
<td>-</td>
<td>40</td>
</tr>
<tr>
<td>Diphenyl dichlorosilane</td>
<td>(C_6H_5)2SiCl_2</td>
<td>193-202 (100 mm)</td>
<td>1.19</td>
<td>-</td>
<td>40</td>
</tr>
<tr>
<td>Diphenyl dichlorosilane</td>
<td>(C_6H_5)2SiCl_2</td>
<td>193 (100 mm)</td>
<td>193</td>
<td>202 (100 mm)</td>
<td>199</td>
</tr>
<tr>
<td>Diphenyl dichlorosilane</td>
<td>(C_6H_5)2SiCl_2</td>
<td>243 (50 mm)</td>
<td>200</td>
<td>-</td>
<td>60</td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Specific Gravity; d) Boiling Point; e) Refractive index; f) Bibliography
<table>
<thead>
<tr>
<th>a) Name;</th>
<th>b) Formula;</th>
<th>c) Boiling point;</th>
<th>d) Specific gravity;</th>
<th>e) Refractive index;</th>
<th>f) Bibliography</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylvinylidichlorosilane</td>
<td>CH₃(CH=CH)SiCl₂</td>
<td>93</td>
<td>1.085</td>
<td>-</td>
<td>39</td>
</tr>
<tr>
<td>Methylallyldichlorosilane</td>
<td>CH₃(CH=CH=CH)SiCl₂</td>
<td>120</td>
<td>1.057</td>
<td>-</td>
<td>39</td>
</tr>
<tr>
<td>Methyllethylidichlorosilane</td>
<td>CH₃(C₂H₅)SiCl₂</td>
<td>100</td>
<td>(744 mm)</td>
<td>-</td>
<td>95</td>
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<tr>
<td>Methylbutylidichlorosilane</td>
<td>CH₃(C₃H₇)SiCl₂</td>
<td>147.5</td>
<td>148</td>
<td>(744 mm)</td>
<td>21.22, 52</td>
</tr>
<tr>
<td>Methylhexylidichlorosilane</td>
<td>CH₃(C₆H₁₃)SiCl₂</td>
<td>204</td>
<td>82.5</td>
<td>(13 mm)</td>
<td>172</td>
</tr>
<tr>
<td>Methylcyclohexylidichlorosilane</td>
<td>CH₃(C₆H₁₀)(CH₂)₂SiCl₂</td>
<td>200—210</td>
<td>1.1876</td>
<td>(20 mm)</td>
<td>21.22, 52</td>
</tr>
<tr>
<td>Ethylcyclohexylidichlorosilane</td>
<td>CH₂(C₆H₁₁)SiCl₂</td>
<td>204</td>
<td>-</td>
<td>(745 mm)</td>
<td>21.22, 52</td>
</tr>
<tr>
<td>Ethylisobutylidichlorosilane</td>
<td>CH₂(C₃H₇)(CH₂)₂SiCl₂</td>
<td>152—154</td>
<td>1.048</td>
<td>195, 196</td>
<td></td>
</tr>
<tr>
<td>Ethylphenylidichlorosilane</td>
<td>C₂H₅(C₆H₅)SiCl₂</td>
<td>105</td>
<td>1.159</td>
<td>-</td>
<td>17.172, 195</td>
</tr>
<tr>
<td>Ethylbenzylidichlorosilane</td>
<td>C₆H₅(C₆H₅)(CH₂)₂SiCl₂</td>
<td>155—156</td>
<td>(100 mm)</td>
<td>-</td>
<td>201</td>
</tr>
<tr>
<td>Propylphenylidichlorosilane</td>
<td>C₆H₅(C₆H₅)SiCl₂</td>
<td>230</td>
<td>1.028</td>
<td>140—144</td>
<td>21, 22</td>
</tr>
<tr>
<td>Phenylbenzylidichlorosilane</td>
<td>C₆H₅(C₆H₅)CH₂SiCl₂</td>
<td>140—144</td>
<td>(100 mm)</td>
<td>-</td>
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<tr>
<td>Phenyltolylidichlorosilane</td>
<td>C₆H₅(C₆H₅)CH₄SiCl₂</td>
<td>318</td>
<td>-</td>
<td>21, 22</td>
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<tr>
<td>Phenylethylidichlorosilane</td>
<td>C₆H₅(C₆H₅)CH₂CH₂SiCl₂</td>
<td>318</td>
<td>-</td>
<td>21, 22</td>
<td></td>
</tr>
<tr>
<td>Phenylcyclohexylidichlorosilane</td>
<td>C₆H₅(C₆H₅)CH₂C₆H₅SiCl₂</td>
<td>224—226</td>
<td>(50 mm)</td>
<td>-</td>
<td>21, 22</td>
</tr>
<tr>
<td>Trimethylchlorosilane</td>
<td>(CH₃)₂SiCl</td>
<td>57.5</td>
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<td>Triethylchlorosilane</td>
<td>(C₂H₅)₃SiCl</td>
<td>143.5</td>
<td>0.925</td>
<td>194</td>
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P-T3-9191/V 470
<table>
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<tr>
<th>a)</th>
<th>b)</th>
<th>c)</th>
<th>d)</th>
<th>e)</th>
<th>f)</th>
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</thead>
<tbody>
<tr>
<td>Tripropylchlorosilane</td>
<td>(C₅H₁₃)₂SiCl</td>
<td>202</td>
<td>1.442</td>
<td>—</td>
<td>21.22</td>
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<td>Triphenylchlorosilane</td>
<td>(C₆H₅)₃SiCl</td>
<td>365</td>
<td>—</td>
<td>40</td>
<td>20.21</td>
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<tr>
<td>Tribenzylchlorosilane</td>
<td>(C₆H₅CH₂)₂SiCl</td>
<td>378</td>
<td>—</td>
<td>—</td>
<td>20.21</td>
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<tr>
<td>Tri-p-tolylchlorosilane</td>
<td>(C₆H₅)₂C₆H₅SiCl</td>
<td>260—300</td>
<td>(150 mm)</td>
<td>—</td>
<td>20.21</td>
</tr>
<tr>
<td>Dimethylethylchlorosilane</td>
<td>(C₂H₅)₂SiCl</td>
<td>20.2</td>
<td>20.21</td>
<td>21.22</td>
<td>218</td>
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<tr>
<td>Dimethylallylchlorosilane</td>
<td>(C₂H₅)₂CH=CH₂SiCl</td>
<td>89—89.2</td>
<td>(734 mm)</td>
<td>—</td>
<td>204</td>
</tr>
<tr>
<td>Methyldiphenylchlorosilane</td>
<td>(C₆H₅)₂C₆H₅SiCl</td>
<td>112</td>
<td>0.922</td>
<td>39.21</td>
<td>218.90</td>
</tr>
<tr>
<td>Diethylpropylchlorosilane</td>
<td>(C₂H₅)₂C₆H₅SiCl</td>
<td>14</td>
<td>—</td>
<td>218.90</td>
<td>203</td>
</tr>
<tr>
<td>Ethyldi-(phenyl)-chlorosilane</td>
<td>C₆H₅(C₆H₅)₂SiCl</td>
<td>116</td>
<td>—</td>
<td>116</td>
<td>203</td>
</tr>
<tr>
<td>Ethyldi-(benzyl)-chlorosilane</td>
<td>C₆H₅(C₆H₅(CH₂)₂SiCl</td>
<td>124—126</td>
<td>(30 mm)</td>
<td>52.53</td>
<td>203</td>
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<tr>
<td>Propyldi-(phenyl)-chlorosilane</td>
<td>C₆H₅(C₆H₅)₂SiCl</td>
<td>88—90</td>
<td>(10 mm)</td>
<td>52.53</td>
<td>203</td>
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<tr>
<td>Dicyclohexyl-(phenyl)-chlorosilane</td>
<td>C₆H₅(C₆H₅(CH₂)₂SiCl</td>
<td>188—192</td>
<td>(0.5 mm)</td>
<td>202</td>
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</tr>
<tr>
<td>Methyl-(propyl)-phenylchlorosilane</td>
<td>CH₂(C₂H₅)₂CH₂SiCl</td>
<td>124—126</td>
<td>(30 mm)</td>
<td>224</td>
<td>203</td>
</tr>
<tr>
<td>Ethyl-(propyl)-phenylchlorosilane</td>
<td>C₆H₅(C₂H₅)₂CH₂SiCl</td>
<td>230—260</td>
<td>(100 mm)</td>
<td>218</td>
<td>203</td>
</tr>
<tr>
<td>Ethyl-(propyl)-benzylchlorosilane</td>
<td>C₆H₅(C₂H₅)₂(C₂H₅CH₂)₂SiCl</td>
<td>178—182</td>
<td>(100 mm)</td>
<td>218</td>
<td>203</td>
</tr>
<tr>
<td>Ethyl-(isobutyl)-benzylchlorosilane</td>
<td>C₆H₅(C₂H₅)₂(C₂H₅CH₂)₂SiCl</td>
<td>174</td>
<td>—</td>
<td>218</td>
<td>203</td>
</tr>
<tr>
<td>Tri-(diacetyl methyl)chlorosilane</td>
<td>[(CH₃CO)₂CH₂]₂SiCl</td>
<td>200</td>
<td>(100 mm)</td>
<td>—</td>
<td>219</td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Boiling point; d) Specific gravity; e) Refractive index; f) Bibliography

F-TS-9191/V 1471
Table 56
Physical Properties of Alkyl-(Aryl)-Bromosilanes and Alkyl-(Aryl)-Iodosilanes

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c)</th>
<th>d)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Formula</td>
<td>°C</td>
<td>n&lt;sub&gt;D&lt;/sub&gt;</td>
</tr>
<tr>
<td>Methyltribromosilane</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;SiBr&lt;sub&gt;3&lt;/sub&gt;</td>
<td>133.5</td>
<td>28.78</td>
</tr>
<tr>
<td>Propyltribromosilane</td>
<td>C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;9&lt;/sub&gt;SiBr&lt;sub&gt;3&lt;/sub&gt;</td>
<td>183</td>
<td>28</td>
</tr>
<tr>
<td>Dimethyl dibromosilane</td>
<td>(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;SiBr&lt;sub&gt;2&lt;/sub&gt;</td>
<td>119</td>
<td>28.78</td>
</tr>
<tr>
<td>Methylmethyldibromosilane</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;(CH&lt;sub&gt;3&lt;/sub&gt;)SiBr&lt;sub&gt;2&lt;/sub&gt;</td>
<td>139-141</td>
<td>28.78</td>
</tr>
<tr>
<td>Diphenyl dibromosilane</td>
<td>(C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;SiBr&lt;sub&gt;2&lt;/sub&gt;</td>
<td>180</td>
<td>136</td>
</tr>
<tr>
<td>Trimethyl bromosilane</td>
<td>(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;SiBr</td>
<td>80</td>
<td>1,148 (25°)</td>
</tr>
<tr>
<td>Triethyl bromosilane</td>
<td>(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;SiBr</td>
<td>162</td>
<td>1,177, 1,458</td>
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<tr>
<td>(24 mm)</td>
<td>66.5</td>
<td>102</td>
<td></td>
</tr>
<tr>
<td>Triallyl bromosilane</td>
<td>(C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;SiBr</td>
<td>213</td>
<td>150.1</td>
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<tr>
<td>Triisobutyl bromosilane</td>
<td>(C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;9&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;SiBr</td>
<td>79</td>
<td>66</td>
</tr>
<tr>
<td>Triisooctyl bromosilane</td>
<td>[(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CHCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub)]SiBr</td>
<td>245</td>
<td>221</td>
</tr>
<tr>
<td>Triphenyl bromosilane</td>
<td>[(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CHCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub])SiBr</td>
<td>278-280</td>
<td>221</td>
</tr>
<tr>
<td>Methyltrioiodosilane</td>
<td>(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;SiI</td>
<td>m.p. 119</td>
<td>78.207</td>
</tr>
<tr>
<td>Propyltrioiodosilane</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;SiI&lt;sub&gt;3&lt;/sub&gt;</td>
<td>229</td>
<td>2,946</td>
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<tr>
<td>Diisopropyltrioiodosilane</td>
<td>[(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CHCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub)]SiI&lt;sub&gt;3&lt;/sub&gt;</td>
<td>252-254</td>
<td>208</td>
</tr>
<tr>
<td>Trimethyl iodosilane</td>
<td>(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;SiI</td>
<td>106.5</td>
<td>208</td>
</tr>
<tr>
<td>Triethyl iodosilane</td>
<td>(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;SiI</td>
<td>193</td>
<td>208</td>
</tr>
<tr>
<td>Triallyl iodosilane</td>
<td>(C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;SiI</td>
<td>235</td>
<td>208</td>
</tr>
<tr>
<td>Methyl disobutyl iodosilane</td>
<td>[(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CHCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub)]SiI&lt;sub&gt;2&lt;/sub&gt;</td>
<td>202-204</td>
<td>208</td>
</tr>
<tr>
<td>Methyl dibutyl iodosilane</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;SiI</td>
<td>148-153</td>
<td>208</td>
</tr>
<tr>
<td>Methyl diphenyl iodosilane</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;(C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;SiI</td>
<td>134-136</td>
<td>208</td>
</tr>
<tr>
<td>Methyl diphenyl iodosilane</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;(C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;SiI</td>
<td>200-204</td>
<td>208</td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Boiling point; d) Specific gravity; e) Refractive index; f) Bibliography
| Table 57 |
| Physical Properties of Alkyl-(aryl)-Fluorosilanes |

<table>
<thead>
<tr>
<th>a) Name</th>
<th>b) Formula</th>
<th>c) Melting point (°C)</th>
<th>d) Boiling point (°C)</th>
<th>e) Specific gravity</th>
<th>f) Refractive index</th>
<th>g) Bibliography</th>
</tr>
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<tbody>
<tr>
<td>Methyltrifluorosilane</td>
<td>CH₃SiF₃</td>
<td>-72,8</td>
<td>-30</td>
<td>-</td>
<td>-</td>
<td>67,72</td>
</tr>
<tr>
<td>Ethyltrifluorosilane</td>
<td>C₂H₅SiF₃</td>
<td>-118,3</td>
<td>-4,2</td>
<td>-</td>
<td>-</td>
<td>56,67</td>
</tr>
<tr>
<td>Propyltrifluorosilane</td>
<td>C₃H₇SiF₃</td>
<td>24,9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>67,70</td>
</tr>
<tr>
<td>Isopropyltrifluorosilane</td>
<td>(CH₃)₂CHSiF₃</td>
<td>-127,6</td>
<td>15,7</td>
<td>-</td>
<td>-</td>
<td>67,76</td>
</tr>
<tr>
<td>Butyltrifluorosilane</td>
<td>C₄H₉SiF₃</td>
<td>96,6</td>
<td>32,4</td>
<td>1,006</td>
<td>-</td>
<td>67,76</td>
</tr>
<tr>
<td>Amyltrifluorosilane</td>
<td>C₅H₁₁SiF₃</td>
<td>77</td>
<td>0,9923</td>
<td>-</td>
<td>-</td>
<td>72</td>
</tr>
<tr>
<td>2-Methylhexyltrifluorosilane</td>
<td>CH₃(CH₂)₃CH₂CH₂CH₂SiF₃</td>
<td>-50</td>
<td>101</td>
<td>0,8376</td>
<td>1,3862</td>
<td>67,68</td>
</tr>
<tr>
<td>Dodecyltrifluorosilane</td>
<td>C₁₂H₂₅SiF₃</td>
<td>-111</td>
<td>-</td>
<td>0,9048</td>
<td>1,212</td>
<td>70,72</td>
</tr>
<tr>
<td>Phenyltrifluorosilane</td>
<td>C₆H₅SiF₃</td>
<td>18,5</td>
<td>102</td>
<td>1,212</td>
<td>(17°)</td>
<td>70,72</td>
</tr>
<tr>
<td>Cyclohexyltrifluorosilane</td>
<td>C₆H₁₂SiF₃</td>
<td>106</td>
<td>1,1012</td>
<td>0,8586</td>
<td>66,61</td>
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</tr>
<tr>
<td>Dimethylidifluorosilane</td>
<td>(CH₃)₂SiF₂</td>
<td>87,5</td>
<td>2,7</td>
<td>-</td>
<td>-</td>
<td>72</td>
</tr>
<tr>
<td>Diethylidifluorosilane</td>
<td>(C₂H₅)₂SiF₂</td>
<td>-78,7</td>
<td>61</td>
<td>0,9267</td>
<td>1,2893</td>
<td>70</td>
</tr>
<tr>
<td>Diisopropylidifluorosilane</td>
<td>[(CH₃)₂CH]₂SiF₂</td>
<td>-100,7</td>
<td>1,3662</td>
<td>-</td>
<td>67,68</td>
<td></td>
</tr>
<tr>
<td>Tributylidifluorosilane</td>
<td>(C₄H₉)₂SiF₂</td>
<td>154</td>
<td>1,8972</td>
<td>-</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td>Dimethylidifluorosilane</td>
<td>(C₃H₇)₂SiF₂</td>
<td>193</td>
<td>(20,5°)</td>
<td>-</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td>Diphenylidifluorosilane</td>
<td>(C₆H₅)₂SiF₂</td>
<td>217</td>
<td>(20,5°)</td>
<td>-</td>
<td>70,72</td>
<td></td>
</tr>
<tr>
<td>Methylphenylidifluorosilane</td>
<td>C₆H₅(C₄H₉)SiF₂</td>
<td>-42,9</td>
<td>1,192</td>
<td>(767°)</td>
<td>70,71</td>
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</tr>
<tr>
<td>Trimethylfluorosilane</td>
<td>(CH₃)₃SiF</td>
<td>-74,3</td>
<td>16,4</td>
<td>-</td>
<td>-</td>
<td>71</td>
</tr>
<tr>
<td>Triethylfluorosilane</td>
<td>(C₂H₅)₃SiF</td>
<td>-102,110</td>
<td>0,8354</td>
<td>1,3915</td>
<td>142</td>
<td></td>
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<tr>
<td>Triisopropylfluorosilane</td>
<td>(C₃H₇)₃SiF</td>
<td>-175</td>
<td>0,8354</td>
<td>1,4118</td>
<td>210</td>
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<tr>
<td>Triisopropylfluorosilane</td>
<td>[(CH₃)₂CH]₂SiF₂</td>
<td>174</td>
<td>0,8339</td>
<td>1,4107</td>
<td>67,66</td>
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</tr>
<tr>
<td>Triphenylfluorosilane</td>
<td>(C₆H₅)₃SiF</td>
<td>169</td>
<td>-</td>
<td>1,4200</td>
<td>67,66</td>
<td></td>
</tr>
<tr>
<td>Triisopropylfluorosilane</td>
<td>[(CH₃)₂CH]₂SiF₂</td>
<td>174</td>
<td>(14,5°)</td>
<td>-</td>
<td>67,66</td>
<td></td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Melting point; d) Boiling point; e) Specific gravity; f) Refractive index; g) Bibliography
<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c)</th>
<th>d)</th>
<th>e)</th>
<th>f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name;</td>
<td>Formula;</td>
<td>Melting point;</td>
<td>Boiling point;</td>
<td>Specific gravity;</td>
<td>Refractive index;</td>
</tr>
<tr>
<td>Triphenylfluorosilane</td>
<td>(C₆H₅)₃SiF</td>
<td>64°</td>
<td>205° (10 mm)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Tribenzylfluorosilane</td>
<td>(C₆H₅CH₂)₂SiF</td>
<td>79°</td>
<td>236° (7,5 mm)</td>
<td>—</td>
<td>—</td>
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<tr>
<td>Methylidipropylfluorosilane</td>
<td>CH₂(C₂H₅)₂SiF</td>
<td>130.2°</td>
<td>1,3942 67,68</td>
<td>(19,0)</td>
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</tr>
<tr>
<td>Methyl diisopropylfluorosilane</td>
<td>CH₃(CH₃)₂CH₂SiF</td>
<td>124.5°</td>
<td>1,3958 67,68</td>
<td>(21)</td>
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</tr>
</tbody>
</table>

Table 58
Physical Properties of Alkyl-(Aryl)-Fluorochlorosilanes

<table>
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<tr>
<th>a)</th>
<th>b)</th>
<th>c)</th>
<th>d)</th>
<th>e)</th>
<th>f)</th>
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<tbody>
<tr>
<td>Name;</td>
<td>Formula;</td>
<td>Melting point;</td>
<td>Boiling point;</td>
<td>Specific gravity;</td>
<td>Refractive index;</td>
</tr>
<tr>
<td>Methyl difluorochlorosilane</td>
<td>CH₃SiF₂Cl</td>
<td>110°</td>
<td>0.5</td>
<td>211</td>
<td></td>
</tr>
<tr>
<td>Methyl fluorodichlorosilane</td>
<td>CH₃SiCl₂</td>
<td>98.7°</td>
<td>29.5</td>
<td>211</td>
<td></td>
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<tr>
<td>Ethyl difluorochlorosilane</td>
<td>C₂H₅SiF₂Cl</td>
<td>Subl.</td>
<td>27.2</td>
<td>1,103</td>
<td>5</td>
</tr>
<tr>
<td>Ethyl fluorodichlorosilane</td>
<td>C₂H₅SiCl₂</td>
<td>62.2°</td>
<td>1,154</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Propyl difluorochlorosilane</td>
<td>C₃H₇SiF₂Cl</td>
<td></td>
<td>70°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propyl fluorodichlorosilane</td>
<td>C₃H₇SiCl₂</td>
<td>88—89°</td>
<td>70°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isopropyl difluorochlorosilane</td>
<td>(CH₃)₂CH₀SiF₂Cl</td>
<td></td>
<td>76°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isopropyl fluorodichlorosilane</td>
<td>(CH₃)₂CH₀SiCl₂</td>
<td>84°</td>
<td>76°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butyl difluorochlorosilane</td>
<td>C₄H₉SiF₂Cl</td>
<td></td>
<td>70°</td>
<td></td>
<td></td>
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<tr>
<td>Butyl fluorodichlorosilane</td>
<td>C₄H₉SiCl₂</td>
<td>110.1°</td>
<td>70°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenyl difluorochlorosilane</td>
<td>C₆H₅SiF₂Cl</td>
<td>79–83°</td>
<td>1,200</td>
<td>71,72</td>
<td></td>
</tr>
<tr>
<td>Phenyl fluorodichlorosilane</td>
<td>C₆H₅SiCl₂</td>
<td>83–86°</td>
<td>1,271</td>
<td>71,72</td>
<td></td>
</tr>
<tr>
<td>Dimethyl fluorochlorosilane</td>
<td>(CH₃)₂SiCl₂</td>
<td>85°</td>
<td>1,181</td>
<td>67°</td>
<td></td>
</tr>
<tr>
<td>Diphenyl fluorochlorosilane</td>
<td>(C₆H₅)₂SiCl</td>
<td>123–125°</td>
<td>71°</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Melting point; d) Boiling point; e) Specific gravity; f) Refractive index; g) Bibliography
### Table 59
Physical Properties of Alkylhalosilanes Containing Hydrogen Attached to the Silicon Atom

<table>
<thead>
<tr>
<th>a) Name</th>
<th>b) Formula</th>
<th>c) Melting point</th>
<th>d) Boiling point</th>
<th>e) Specific gravity</th>
<th>f) Refractive index</th>
<th>g) Bibliography</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl trifluorosilane</td>
<td>CH₃SiHF₂</td>
<td>-110±0.5</td>
<td>-37.6</td>
<td></td>
<td>69</td>
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</tr>
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<td>Methyl fluorochlorosilane</td>
<td>CH₃SiHCl</td>
<td>-120±0.5</td>
<td>1.2±1</td>
<td>1.059</td>
<td></td>
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<tr>
<td>Methylchlorosilane</td>
<td>CH₃SiHCl</td>
<td></td>
<td>134</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl dichlorosilane</td>
<td>CH₃SiCl₂</td>
<td></td>
<td>-90.6±0.5</td>
<td>40.4±0.1</td>
<td>1.105</td>
<td>214</td>
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<td>Ethyl dichlorosilane</td>
<td>C₂H₅SiHCl</td>
<td>74.9</td>
<td>75.4</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Allyldichlorosilane</td>
<td>C₃H₇SiHCl</td>
<td></td>
<td>97</td>
<td>1.1086</td>
<td>212.213</td>
<td></td>
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<tr>
<td>Phenyl dichlorosilane</td>
<td>C₆H₅SiHCl₂</td>
<td>65~65.3 (10 mm)</td>
<td>98</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Benzyldichlorosilane</td>
<td>C₆H₅CH₂SiHCl₂</td>
<td>33.55 (6 mm)</td>
<td>48</td>
<td>1.1770</td>
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<tr>
<td>p-Tolyl dichlorosilane</td>
<td>C₆H₅SiHCl₂</td>
<td></td>
<td></td>
<td>1.5246</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Chlorophenyl dichlorosilane</td>
<td>C₆H₅ClSiHCl₂</td>
<td>115~100 (20 mm)</td>
<td></td>
<td>1.5431</td>
<td>18.8</td>
<td></td>
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<tr>
<td>Dodecyl dichlorosilane</td>
<td>C₁₂H₂₅SiHCl₂</td>
<td>150~156 (15 mm)</td>
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<tr>
<td>Tetradecyl dichlorosilane</td>
<td>C₁₄H₂₉SiHCl₂</td>
<td>142~146 (2 mm)</td>
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<td></td>
<td></td>
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<tr>
<td>Octadecyl dichlorosilane</td>
<td>C₁₈H₃₇SiHCl₂</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-Naphthyldichlorosilane</td>
<td>C₁₀H₃SiHCl₂</td>
<td>146.2~147.5 (10 mm)</td>
<td></td>
<td>1.6140</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diethyl dichlorosilane</td>
<td>(C₂H₅)₂SiHCl</td>
<td>93.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diphenyl dichlorosilane</td>
<td>(C₆H₅)₂SiHCl</td>
<td>140~145 (7 mm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dibenzyl dichlorosilane</td>
<td>[C₆H₅(CH₃)₂]SiHCl</td>
<td>35</td>
<td>155~161 (6 mm)</td>
<td>1.0853</td>
<td>2.5734</td>
<td>18</td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Melting point; d) Boiling point; e) Specific gravity; f) Refractive index; g) Bibliography
**Table 60**

Dipole Moments of Alkyl-(Aryl)-Halosilanes

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c)</th>
<th>d)</th>
<th>e)</th>
<th>f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triethylchlorosilane</td>
<td>(C₆H₅)₂SiCl</td>
<td>2.07</td>
<td>(CH₂)Cl</td>
<td>2.15</td>
<td>86</td>
</tr>
<tr>
<td>Diethylchlorosilane</td>
<td>(C₆H₅)₂SiCl₂</td>
<td>2.39</td>
<td>(CH₂)C₂Cl₂</td>
<td>1.99</td>
<td>86</td>
</tr>
<tr>
<td>Ethyltrichlorosilane</td>
<td>C₆H₅SiCl₂</td>
<td>2.04</td>
<td>CH₂C₂Cl₂</td>
<td>1.60</td>
<td>86</td>
</tr>
<tr>
<td>Triphenylchlorosilane</td>
<td>(C₆H₅)₂SiCl</td>
<td>2.14</td>
<td>—</td>
<td>—</td>
<td>217</td>
</tr>
<tr>
<td>Diphenyldichlorosilane</td>
<td>(C₆H₅)₂SiCl₂</td>
<td>2.56</td>
<td>(C₆H₅)₂C₂Cl₂</td>
<td>2.39</td>
<td>217</td>
</tr>
<tr>
<td>Phenyltrichlorosilane</td>
<td>C₆H₅SiCl₂</td>
<td>2.84</td>
<td>C₆H₅C₂Cl₂</td>
<td>2.04</td>
<td>217</td>
</tr>
<tr>
<td>Triethylfluorosilane</td>
<td>(C₆H₅)₂SiF</td>
<td>1.72</td>
<td>(C₆H₅)₂CH₂Cl</td>
<td>1.92</td>
<td>217</td>
</tr>
<tr>
<td>Diethyl trifluorosilane</td>
<td>(C₆H₅)₂SiF₂</td>
<td>2.33</td>
<td>—</td>
<td>—</td>
<td>217</td>
</tr>
<tr>
<td>Triphenyldifluorosilane</td>
<td>(C₆H₅)₂SiF</td>
<td>2.84</td>
<td>(C₆H₅)₂CH₂Cl</td>
<td>1.77</td>
<td>217</td>
</tr>
<tr>
<td>Dichlorosilane</td>
<td>SiCl₂</td>
<td>1.28</td>
<td>CH₂Cl</td>
<td>1.87</td>
<td>217</td>
</tr>
<tr>
<td>Chlorosilane</td>
<td>(SiCl₄)</td>
<td>2.77</td>
<td>(C₆H₅)₂CH₂Cl</td>
<td>2.56</td>
<td>217</td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Dipole moment, 10⁻¹⁸ ESU; d) Formula of corresponding organic compounds; e) Dipole moment, 10⁻¹⁸ ESU; f) Bibliography

**Table 61**

Boiling Points of Azeotropic Mixtures of Chlorosilanes with Certain Compounds (Bibl.34, 35)

<table>
<thead>
<tr>
<th>Component 1</th>
<th>Component 2</th>
<th>BP of Mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiCl₄</td>
<td>(CH₂)₂SiCl</td>
<td>54.3</td>
</tr>
<tr>
<td>SiCl₄</td>
<td>CH₂CN</td>
<td>48.6</td>
</tr>
<tr>
<td>SiCl₄</td>
<td>CH₃CN</td>
<td>51.2</td>
</tr>
<tr>
<td>(CH₂)₃SiCl</td>
<td>CH₃CN</td>
<td>66.6</td>
</tr>
<tr>
<td>(C₆H₅)₂SiCl</td>
<td>CH₃CN</td>
<td>57.3</td>
</tr>
</tbody>
</table>

**Table 62**

Physical Properties of Methyl and Ethylchlorosilanes

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c)</th>
<th>d)</th>
<th>e)</th>
<th>f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyltrichlorosilane</td>
<td>CH₃SiCl₂</td>
<td>64.6</td>
<td>9.3</td>
<td>8.4</td>
<td>54</td>
</tr>
<tr>
<td>Dimethyl dichlorosilane</td>
<td>(CH₃)₂SiCl</td>
<td>69.4</td>
<td>9.7</td>
<td>10</td>
<td>48</td>
</tr>
<tr>
<td>Ethyltrichlorosilane</td>
<td>C₆H₅SiCl₂</td>
<td>92</td>
<td>14</td>
<td>14</td>
<td>48</td>
</tr>
<tr>
<td>Diethyl dichlorosilane</td>
<td>(C₆H₅)₂SiCl₂</td>
<td>90</td>
<td>26</td>
<td>13</td>
<td>26</td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Boiling point; d) Flash point; e) Fire point; f) Vapor pressure (mm Hg) of pure products at temperatures, °C
Chemical Properties of Alkyl-(Aryl)-Halosilanes

Reactions Connected with the Replacement of a Halogen Atom Bound to a Silicon Atom

The halogen atoms in alkyl-(aryl)-halosilanes maintain the same chemical character as in the tetrahalosilanes (which, as pointed out above, are typical inorganic acid chlorides). The organic radicals screen the bond between the halogen atom and the silicon atom, and therefore the activity of the halogen atom is more or less lowered. In the lower alkylhalosilanes (for instance in the methylchlorosilanes) this influence is only faint, and as a whole, the compound maintains the pronounced character of an acid chloride; it is instantaneously hydrolyzed by water, it reacts actively with hydroxyl-containing compounds etc. In alkylhalosilanes containing high-molecular radicals, and in particular radicals with a branched structure, the weakening in the mobility and activity of the halogen atom attached to the silicon atom is expressed considerably more strongly. Thus, for instance, tert-butyltrichlorosilane reacts only weakly with water.

The most important reaction in the chemistry of organosilicon compounds is the reaction of hydrolysis of alkyl-(aryl)-halosilanes, which proceeds in the first instant in the same direction as the reaction of hydrolysis of tetrahalosilanes:

\[
\text{Si} X + \text{H}_2\text{O} \rightarrow \text{Si} \text{OH} + \text{HX}
\]

The hydrolysis of alkyl-(aryl)-halosilanes, the processes of condensation accompanying hydrolysis, the structure and properties of the reaction products are discussed in detail below (cf. pp. 529 et seq.).

The reaction between alkyl-(aryl)-halosilanes with hydroxyl-containing organic compounds may proceed by the two schemes described for the tetrahalosilanes: by the scheme of hydrolysis

\[
\text{Si} X + \text{HO} \rightarrow \text{Si} \text{OH} + \text{XC}
\]

by the scheme of esterification

F-TS-9191/V 477
While the tetrahalosilanes react with equal ease by the first and second patterns, in the case of the alkylhalosilanes it is far easier to conduct the process of esterification.

The Reaction of Esterification

The reaction between alkyl-(aryl)-chlorosilanes with alcohol takes place according to the pattern:

\[
RXSiCl_{4-x} + (4-x)ROH \rightarrow R_xSi(OR')_{4-x} + (4-x)HCl
\]

The basic factors determining the process of the reaction between alkyl-(aryl)-chlorosilanes and alcohols is the size of the alcohol radical, and also the size and number of organic radicals attached to the silicon atom.

The activity of the alkylchlorosilanes in the reaction of esterification is considerably less than that of SiCl₄. Thus, for example, even when methyltrichlorosilane reacts with absolute ethanol, the thermal effect and the velocity of the process are considerably lower than for the corresponding reaction with SiCl₄. Ethyltrichlorosilane reacts still more slowly, and for the esterification, for instance, of diphenyldichlorosilane, it must be heated for 6-8 hours (Bibl.87). In the case that the radical of the alkyl-(aryl)-chlorosilane or alcohol radical R' is a sufficiently long or branched hydrocarbon chain or ring, the velocity and intensity of the esterification reaction are very small. For instance (Bibl.88), diphenyldichlorosilane reacts with phenyl only at 200°C. When heated for 8 hours a mixture is formed containing not only a substituted ester, but an arylhalo ester:

\[
(C_6H_5)SiCl_2 + C_6H_5OH \rightarrow (C_6H_5)_3SiCl(C_6H_5OH) + HCl
\]

\[
(C_6H_5)SiCl(OCC_6H_5) + C_6H_5OH \rightarrow (C_6H_5)_3Si(OCC_6H_5) + HCl
\]
The esterification of alkylchlorosilanes by the lower alcohols, like the reaction of esterification of SiCl₄, always proceeds with the formation of a certain quantity of polymeric hydrolysis products (owing to the cleavage of water from the reaction between the HCl and the alcohol). For instance, in the esterification of diethylidichlorosilane, the following side reactions take place together with the main reactions (Bibl.89):

\[
\begin{align*}
\text{HCl} + \text{C}_2\text{H}_5\text{OH} & \quad \rightarrow \quad \text{C}_2\text{H}_5\text{Cl} + \text{H}_2\text{O} \\
2\text{C}_2\text{H}_5\text{SiCl}_2 + \text{H}_2\text{O} & \quad \rightarrow \quad (\text{C}_2\text{H}_5\text{SiCl}_2)\text{Cl} + 2\text{HCl} \\
(\text{C}_2\text{H}_5\text{SiCl}_2)\text{Cl} + 2\text{C}_2\text{H}_5\text{OH} & \quad \rightarrow \quad (\text{C}_2\text{H}_5\text{Si} - \text{O} - \text{Si}(\text{C}_2\text{H}_5)_2 + 2\text{HCl} \\
\text{OC}_2\text{H}_5 & \quad \text{OC}_2\text{H}_5
\end{align*}
\]

If the esterification is conducted by the action of an alcoholate (instead of an alcohol), the formation of polymeric products of hydrolysis is theoretically impossible, but the yield of substituted esters is low. Thus, for instance (Bibl.90) when a mixture of 3 mols of sodium ethylate and 1 mol of ethyltrichlorosilane is boiled, ethyltriethoxysilane in 40% yield is formed. The reaction with sodium methylete is of practical importance, and proceeds with somewhat better yields. Ethyltrichlorosilane and sodium methylete give ethyltrimethoxysilane in 50% yield, while diethylidichlorosilane gives diethylidimethoxysilane in 70% yield.

**The Reaction of Acylation**

The replacement of a chlorine atom in tetrahalosilanes by an acid radical RCOO- may be accomplished by reacting the halosilane with an organic acid or its salt. In the case of alkyl-(aryl)-chlorosilanes, it is more convenient to conduct this reaction with the salt of the organic acid, for instance with sodium or silver acetate (Bibl.90):

\[
\begin{align*}
\text{R}_x\text{SiCl}_{4-x} + (4-x)\text{CH}_3\text{COONa} & \quad \rightarrow \quad \text{R}_x\text{Si(OOCCH}_3)_x \quad + \quad (4-x)\text{NaCl}
\end{align*}
\]

**Method of Preparing Alkylacetoxyisilane.** In a flask provided with a stirrer, sodium acetate in 1-5 parts by volume of diluent (benzene, petroleum ether) is placed,
and then a solution of alkylchlorosilane in benzene or petroleum ether (1:1) is added with stirring at the boiling point. The sodium acetate is taken in double the theoretical quantity (for the reaction presented above). The reaction product is separated by filtration and rectified.

With the lower alkylchlorosilanes, this reaction proceeds very vigorously. The alkylchlorosilanes with a long carbon chain (more than 8 carbon atoms) react in a solvent at 60-120°C in 10-20 hours (Bibl.92).

The reaction products are readily hydrolyzed by water, forming polyorganosiloxanes or hydroxysilanes. The latter are best prepared by hydrolysis by means of a sodium carbonate solution:

\[2(R_1H)_2SiOCOCR_2H_5 + Na_2CO_3 + H_2O \rightarrow 2(R_1H)_2Si(OH) + 2R_1COONa + CO_2\]

The practical importance of compounds of the type \(R_xSi(COOE)_{1-x}\) is that, on their hydrolysis, in contrast to the hydrolysis of the allylchlorosilanes, such chemically active by-products as HCl are not formed, while the hydrolysis of such compounds proceeds at a far higher velocity than the hydrolysis of the substituted esters.

The use of such products is recommended for making various materials that cannot be put in contact with HCl water-repellent for instance textiles, paper, etc.

There is a description of the reaction between triethylchlorosilane and the sodium derivative of acetoacetic ester:

\[\text{CH}_3\text{C}=\text{C}=\text{C}\text{H}_5+\text{SiCl}_3 + \text{Na}^+\text{O}^-(\text{COE})_2\rightarrow \text{CH}_3\text{C}=\text{C}=\text{C}\text{H}_5+\text{Na}^+\text{COO}^-(\text{C}_2\text{H}_5)_2+\text{Si}^+\text{O}^-(\text{C}_2\text{H}_5)_3\]

The reaction product is hydrolyzed on treatment with 10% HCl, forming hexaethyl-disiloxane, ethanol, carbon dioxide, and acetone.

\(\text{Action with Ammonia and Nitrogen-Containing Compounds}\)

The reaction between alkyl-(aryl)-halosilanes and ammonia may lead to the form-
ation of the initial substitution products, amines:

\[
-Si-Cl + 2NH_3 \rightarrow -Si-NH_2 + NH_4Cl
\]

and to the condensation products of those amines:

\[
2-Si-NH_2 \rightarrow -Si-NH-Si- + NH_3
\]

Amines may undergo condensation on heating, forming polysilanimines, as the hydroxysilanles will form polksiloxanes. In this way the tendency to polymeric compounds is inherent not only in oxygen-containing organosilicon compounds, but also in such compounds containing nitrogen (also in those containing sulfur). But both nitrogen and sulfur-containing polymers differ from the polyorganosiloxanes in their instability to the action of moisture, and are readily hydrolyzed to polyorganosiloxanes.

By the reaction of trialkyl-(aryl)-chlorosilanes with ammonia, trialkylaminosilanes are usually formed:

\[
R_3SiCl + NH_3 \rightarrow R_3SiNH_2 + NH_4Cl
\]

The preparation of trimethylaminosilane (Bibl.66) is described on page 623.

The reaction between trimethylchlorosilane and ammonia (Bibl.93), in contrast to that of other trialkylchlorosilanes, leads to the formation only of hexamethylaminodisilane:

\[
2(CH_3)_3SiCl + 3NH_3 \rightarrow (CH_3)_6SiNHSi(CH_3)_2 + 2NH_4Cl
\]

**Preparation of Hexamethylaminodisilane.** To 900 ml of liquid ammonia placed in a Dewar vessel, 269 g of trimethylchlorosilane is added, with stirring, over a period of 3 hours and 15 minutes; the excess of ammonia is gradually driven off by heating, after which the hexamethylaminodisilane is isolated by rectification. Its boiling point is 125.7-126.2°C (758 mm). Yield 99 g, or 1.5% of theoretical.

Even when the reaction is conducted at a temperature of -70°C, trimethylamino-
silane is not formed.

Under the action of ammonia on dimethyldichlorosilane (Bibl. 94), dimethyldi-
aminosilane is formed at the initial instant:

\[(\text{CH}_3)_2\text{SiCl}_2 + 4\text{NH}_3 \rightarrow (\text{CH}_3)_2\text{Si}((\text{NH}_3)_2 + 2\text{NH}_4\text{Cl})\]

and is then condensed, forming cyclic polyorganosilanes; in this case the reac-
tion products consist mainly of cyclo-2,4,6-triamino-1,3,5-hexamethyltrisilane and
cyclo-2,4,6,8-tetraimino-1,3,5,7-octamethyltetrasilane:

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{Si} & \quad \text{H}_2\text{C} \\
\text{H} &= \text{N} & \quad \text{H} \\
\text{H}_2\text{C} & \quad \text{Si} & \quad \text{H}_2\text{C} \\
\text{H}_2\text{C} & \quad \text{Si} & \quad \text{H}_2\text{C} \\
\end{align*}
\]

Preparation of Cyclic Aminosilanes. A solution of 903 g of dimethyldichlorosilane in 3 kg of benzene is placed in a round-bottomed flask provided with a stirrer. Ammonia is passed in for 4 hours over the surface of the liquid, with stirring, at a temperature not over 30°C. The ammonium chloride is then filtered off, and the filtrate is again treated with ammonia at the boiling point for 2 hours. Fractionation of the reaction products yields: cyclo-2,4,6-triamino-1,3,5-hexamethyltrisilane, boiling point 188°C (763 mm), and cyclo-2,4,6,8-tetraimino-1,3,5,7-octamethyltetrasilane, boiling point 225°C (765 mm), melting point 97°C.

The reaction between alkylchlorosilanes and ammonia (Bibl. 93, 95) leads to the formation of the respective alkyl-(arylamine)-silanes:

\[(\text{CH}_3)_3\text{SiCl} + 2\text{RNH}_2 \rightarrow (\text{CH}_3)_3\text{SiNHR} + \text{RNH}_4\text{Cl}\]

The process is conducted by poutting the trimethylchlorosilane into an excess of the amine in ether solution. The yield of trimethylmethylaminosilane from methyl-
amine and trimethylchlorosilane is 38%. The yield of trimethylthyleaminosilane
under similar conditions does not exceed 25%. In case the silicon is bound to methyl radicals, it is relatively easy to replace the three hydrogen atoms attached to the nitrogen, forming hexamethylmethyleniminodisilane:

$$(\text{CH}_3)_3\text{SiNHCH}_3 + (\text{CH}_3)_3\text{SiCl} \rightarrow [(\text{CH}_3)_3\text{Si}]_2\text{NCH}_3 + 3\text{HCl}$$

Compounds with other radicals attached to the silicon atom react according to this pattern only on heating.

On the reaction of alkyl-(aryl)-chlorosilanes with silver isocyanate, the corresponding isocyanates are formed (Bibl.96).

$$R_x\text{Si}(\text{Cl})_{4-x} + (4-x)\text{AgNCO} \rightarrow R_x\text{Si}(\text{NCO})_{4-x} \cdot (4-x)\text{AgCl}$$

Alkyl-(aryl)-isothiocyanatosilanes are prepared similarly.

Reactions with Metallic Sodium

Silicon tetrachloride, as already stated, is stable to the action of metallic sodium even at very high temperatures. Alkyl-(aryl)-chlorosilanes prove to be more active in reaction with sodium. When alkyl-(aryl)-chlorosilanes are heated with sodium at 110-140°C, condensation takes place:

$$\text{R}_x\text{Si}(\text{Cl})_{4-x} \rightarrow \text{R}_x\text{Si}(\text{Cl})_{4-x} + 2\text{NaCl}$$

The products of the reaction may either be derivatives of disilane or polyalkyl-(aryl)-silanes of relatively high molecular weight.

Preparation of Hexaalkyl-(Aryl)-Disilane (Bibl.97). When a mixture of 3 g of triphenylchlorosilane dissolved in 150-200 ml of xylene is boiled with 2-3 g of sodium for 2 hours in an atmosphere of nitrogen, hexaphenyldisilane is formed. It is a crystalline substance of melting point 354°C.

By a similar reaction, hexaethylidisilane is formed from triethylbromosilane. By the reaction between phenylethylbromochlorosilane and sodium, diphenyldiethyldi-
propyldisilane is formed. This is a very stable compound which does not decompose even under the action of hot 5% alkali.

An example of the formation of a polymer containing several Si-Si bonds is the preparation of the so-called "tetrane" (Bibl.98).

\[
(C_6H_5)_4SiCl_2 + 8NaCl \rightarrow (C_6H_5)_4Si + 8NaCl
\]

The reaction proceeds under the action of sodium on a toluene solution of diphenyltrichlorosilane at the boiling point, with vigorous stirring of the mixture. The reaction is exothermic, and after it begins no further heating of the mixture is required. From a whole series of reaction products (which are probably polymer homologs) two octaphenyltetrasilanes have been isolated and studied, one of them being stable and apparently having a cyclic structure. The structure of the second, unsaturated compound, cannot be considered to have been definitively established.

Under the action of water, in presence of pyridine, on the unsaturated compound, hydrogen is given off (Bibl.99):

\[
(C_6H_5)_4Si + 8H_2O \rightarrow 4H_2 + 4(C_6H_5)_4Si(OH)_2
\]

The cyclic octaphenyltetrasilane is relatively stable in the air; oxidation was observed under the influence of atmospheric oxygen in boiling toluene or when heated to 100°C for a prolonged period. It also breaks down in benzene solution on distillation; the solution in biphenyl is more stable. Oxygen compounds, such as benzyl alcohol, acetophenone, or amyl nitrite, break it down (it is possible that a transfer of oxygen takes place).

According to Kipping, octaphenyltetrasilane has the following structure:

```
\[
\begin{array}{c}
\text{C}_6\text{H}_5 \\
\text{Si} \\
\text{C}_6\text{H}_5 \\
\text{Si} \\
\text{C}_6\text{H}_5 \\
\text{Si} \\
\text{C}_6\text{H}_5 \\
\text{Si} \\
\text{C}_6\text{H}_5 \\
\end{array}
\]
```

The iodine derivative of octaphenyltetrasilane reacts with a Grignard reagent accord-
ing to the equation:

\[
(C_6H_5)_8Si_4J_2 + C_6H_6MgBr \rightarrow (C_6H_5)_8Si_4(C_6H_5)J + MgBr
\]

(crustals of melting point 253-254°C). The oxide of octaphenyltetrasilane, 
\((C_6H_5)_8SiO_4\), is obtained as a by product. Octaphenyl-diiodotetrasilane loses all its iodine on contact with sodium.

When diphenyl-dichlorosilane or di-p-tolydichlorosilane reacts with KOH, two products are formed, one insoluble and the other soluble in benzene (Bibl.100). The soluble compound obtained from diphenyl-dichlorosilane, had a molecular weight of about 3900, while that prepared from di-p-tolydichlorosilane had 4150. The molecular weight of the insoluble product prepared from di-p-tolydichlorosilane, was 3450.

On the reaction of sodium with dibenzyldichlorosilane in a toluene medium, in a nitrogen atmosphere, followed by addition of KOH, a small quantity of hexabenzyl-disiloxane and tetrabenzylsilane were formed. The principal product of the reaction was a heavy oil, which on analysis was found to be the oxide of octabenzyltetrasilane which was apparently formed on account of the admixture of sodium peroxide in the sodium.

\[
(C_6H_5CH_2)SiCl_3 + 2Na \rightarrow (C_6H_5CH_2)Si(Na)Cl_2 + C_6H_5CH_2Na
\]

\[
(C_6H_5CH_2)SiCl_3 + 2C_6H_5CH_2Na \rightarrow 2NaCl + (C_6H_5CH_2)SiCl
\]

\[
(C_6H_5CH_2)SiCl_3 + C_6H_5CH_2Na \rightarrow NaCl + (C_6H_5CH_2)SiCl
\]

\[
2(C_6H_5CH_2)SiCl + Na_2O \rightarrow 2NaCl + [(C_6H_5CH_2)Si]_2O
\]

Under the action of metallic sodium on dimethyldichlorosilane, high-molecular polydimethylsilane may be obtained:

\[
x(CH_3)SiCl_x + 2xNa \rightarrow [(CH_3)Si]_x + 2xNaCl
\]

Preparation of Polydimethylsilane (Bibl.101). A mixture of 450 g of metallic sodium, 700 g of dimethyldichlorosilane, and 1 liter of benzene, is placed in a 3-liter autoclave. The reaction begins only after the temperature has been brought
up to the melting point of sodium (980°C), and continues with great exothermic effect (spontaneous rise of temperature to 700°C and of pressure to 16 atm). To complete the reaction, the autoclave is heated at 1150°C for 10 hours, after which it is opened and the reaction mass mixture is filtered and distilled. The residue on the filter is blue, probably owing to the presence of the organosilicon radical R₂SiONa. When the precipitate is washed with water, a white powder is separated, whose elementary analysis corresponds to the formula [(CH₃)₂Si]ₓ. According to ebullioscopic determination of the molecular weight, x = 55. X-ray study of the polymer indicates the presence of crystalline structural cells.

The filtrate after the separation of the precipitate is distilled under reduced pressure; from the distillate boiling up to 170°C (2 mm), cyclodidecamethylhexasilane may be isolated. After recrystallization from a water-methanol mixture, the product begins to melt at 74°C and may be sublimed at 100°C. The distillation residue in the retort is of the consistency of grease.

The polymers so obtained are rather stable, and remain unhydrolyzed, not only under the action of water, but even under the action of moist piperidine, which usually causes quantitative cleavage of the Si-Si bond. The quantitative decomposition of the polymers, with liberation of 1 mol of hydrogen for each Si-Si bond, takes place only under the action of hot alkali.

In all the above described reactions between organochlorosilanes and metallic sodium, the process of formation of the Si-Si bond proceeds obviously by analogy to the corresponding reaction of organic haloderivatives:

\[ \text{SiCl}_4 + 2\text{Na} \rightarrow \text{Si} - \text{Na} + \text{NaCl} \]

\[ \text{Si} - \text{Na} + 1.5\text{SiH} \rightarrow \text{Si} - \text{Si} - \text{Na} + \text{H} \]

Triethylbromosilane reacts with sodiumtriphenylgermanium with the formation of an unstable compound (crystals, melting point 93.5°C), which in turn reacts with
metallic lithium, forming triethyllithiumsilane (Bibl.192):

\[
\text{[(C}_2\text{H}_5\text{)}_3\text{SiBr} + (\text{C}_4\text{H}_9)_3\text{Na} \rightarrow \text{NaBr} + (\text{C}_4\text{H}_9)_3\text{Si-Ge(C}_4\text{H}_9)_3
\]

When the mixture so obtained is treated with an alcoholic solution of ammonium bromide, triethylsilane is formed:

\[
\text{[(C}_2\text{H}_5\text{)}_3\text{SiH} + \text{NH}_3\text{Br} \rightarrow (\text{C}_2\text{H}_5)_3\text{SiH} + \text{NH}_3 + \text{LiBr}}
\]

Reactions of Hydrogenation

Patent data (Bibl.103) indicate the possibility of the replacement of a chlorine atom in an alkylchlorosilane by hydrogen, by passing a mixture of the alkylchlorosilane vapor and hydrogen through tablets of silicon containing aluminum chloride at 310-315°C.

Reaction with Sulfuric Acid (Bibl.104)

When 9.8 g of concentrated sulfuric acid is poured into 23.8 g of trimethylchlorosilane with cooling and stirring, the following reaction takes place:

\[
\text{[(CH}_3\text{)}_3\text{SiCl} + \text{H}_2\text{SO}_4 \rightarrow (\text{CH}_3\text{)}_3\text{SiOSO}_3\text{H} + \text{HCl}}
\]

Trimethylsilane sulfate consists of crystals that fume in air and have a melting point of 45-46°C and a boiling point of 87-89°C (h m).

Reactions with Oxides of Metals

When alkyl-(aryl)-chlorosilanes react with metallic oxides (Bibl.105), polyorganosiloxanes may be obtained, for instance:

\[
3(\text{C}_3\text{H}_9\text{SiCl}_2) + 3\text{H}_2\text{O} \rightarrow [(\text{C}_3\text{H}_9\text{Si})_3\text{O}]_3 + 3\text{H}_2\text{Cl}_2
\]
Dimethyldichlorosilane, on reaction with metallic oxides, yields a mixture of various polydimethylsiloxanes.

Alkylchlorosilanes may react with polyalkylsiloxanes (Bibl.96, 106), and in this case the siloxane bond of the latter is broken according to the reaction:

\[
R_2SiCl_2 + OSi(R_2)_n \rightarrow Cl-Si(R_2)_n + R_2SiCl
\]

**Reaction with Sodium Trimethylsilanolate**

As a result of the reaction of sodium trimethylsilanolate with alkylhalosilanes (according to the type of the Williamson reaction), polyorganosiloxanes are formed (Bibl.107):

\[
R_xSiCl_{4-x} + (4-x)(CH_3)_2SiONa \rightarrow R_xSi[(CH_3)_2SiO]_{4-x} \cdot (4-x)NaCl
\]

In this way, the following compounds have been synthesised:

diethyldi- (trimethylsiloxy) -silane \((C_2H_5)_2Si[OSi(CH_3)_3]_2\) - (I),

ethyltri- (trimethylsiloxy) -silane \(C_2H_5Si[OSi(CH_3)_3]_3\) - (II) and
tetra- (trimethylsiloxy) -silane \(Si[OSi(CH_3)_3]_4\) - (III).

Product III may also be prepared by cohydrolysis of \(Si(OC_2H_5)_4\) and \((CH_3)_3SiOC_2H_5\) in an alkaline medium, and also by the reaction of trimethylhydroxysilane and tetraethoxysilane in the presence of metallic sodium:

\[
4(ClH_3)Si(OH) \cdot (C_2H_5O)SiO \rightarrow Na^+ \rightarrow Si[OSi(CH_3)_3]_4 \cdot 4C_2H_5OH
\]

**Preparation of Tetra- ( trimethylsiloxy) -Silane.** To a 10% solution of trimethylsilanol (1.2 mol) in benzene, 1.3 mol of metallic sodium is gradually added. After completion of the reaction (heating is required at the end of the process) the solution of trimethylsilanolate is decanted with the excess of metallic sodium, and SiCl_4 is added to the solution gradually, with cooling and vigorous stirring.

After 40 hours of boiling, the reaction products are washed with water to re-
move the sodium chloride, and the organic layers, after drying over potassium carbonate, is fractionated.

When this reaction is conducted in ether, low yields of the product are observed, owing to the low boiling point of the solvent.

A mixture of 0.2 mol of tetraethoxysilane, 1 mol of trimethylsilanol, and 0.2 g of sodium, is boiled under a reflux condenser for 22 hours, and is then fractionated. The yield of the product III is 18%.

<table>
<thead>
<tr>
<th>Properties of Products I, II, III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling Point, °C (733 mm)</td>
</tr>
<tr>
<td>I  187</td>
</tr>
<tr>
<td>II 206</td>
</tr>
<tr>
<td>III 220</td>
</tr>
<tr>
<td>Refractive Index n²₀</td>
</tr>
<tr>
<td>I  1.4005</td>
</tr>
<tr>
<td>II 1.3944</td>
</tr>
<tr>
<td>III 1.3895</td>
</tr>
<tr>
<td>Specific Gravity</td>
</tr>
<tr>
<td>0  0.8751</td>
</tr>
<tr>
<td>20 0.8599</td>
</tr>
<tr>
<td>60 0.8035</td>
</tr>
<tr>
<td>Viscosity, Centipoises, at °C</td>
</tr>
<tr>
<td>0  2.020</td>
</tr>
<tr>
<td>20 1.441</td>
</tr>
<tr>
<td>60 0.841</td>
</tr>
<tr>
<td>Yield, % of Theoretical</td>
</tr>
<tr>
<td>52</td>
</tr>
<tr>
<td>44</td>
</tr>
<tr>
<td>38</td>
</tr>
</tbody>
</table>

A reaction similar to the above proceeds readily without use of catalysts when the reaction mixture is heated in a steel bomb lined with copper.

When 725 g of dimethyldichlorosilane and 702 g of the hydrolysis product of dimethyldichlorosilane, containing an admixture of 2.5% of methyltrichlorosilane, is heated 5 hours in a bomb at 380-400°C, a mixture of the following percentage composition is formed:

\[ \{ (\text{CH}_3)_2\text{SiO}_3 \} \cdots 0.2 \quad \text{Cl}(\text{CH}_3)_3\text{SiO}(\text{CH}_3)\text{Cl} \cdots 2.12 \]
In a glass bomb the process proceeds less intensely, and conversion under similar conditions is only 21%.

When dry HCl or HBr is used as a catalyst, the reaction may be conducted at room temperature.

Reaction of Thermal Rearrangement of Alkyl-(Aryl)-Chlorosilanes

One of the most interesting and characteristic reactions of the alkylchlorosilanes is thermal rearrangement. In contrast to the reactions described above, the Si-C bonds are broken in thermal rearrangement, and cleavage of the hydrocarbon radicals from some silicon atoms, with their addition to others, takes place:

\[ 2R_2SiCl_2 \rightleftharpoons RSiCl_3 + R_3SiCl \]
\[ 2RSiCl_2 \rightleftharpoons SiCl_4 + R_2SiCl_2 \]

The process is completely reversible, and by studying the equilibrium concentrations, the equilibrium constants for the reactions of rearrangement (disproportionation) may be easily determined.

The phenomenon of disproportionation of hydrocarbon radicals attached to the silicon atom was first observed by Ladenburg, who prepared small amounts of diethyl-diphenylsilane and tetraethylsilane by reacting diethylzinc with phenyltrichlorosilane at 175°C.

Dolgov and Vol'nov (Bibl.109) observed rearrangement on heating organochlorosilanes 24-48 hours in a hydrogen atmosphere at 300°C, under 100 atm pressure. They also noted that, under these conditions, the cleavage of the Si-C bond and the formation of disilane and the hydrocarbon is observed. The rearrangement of alkyl groups in tetraalkylsilanes has also been observed by other authors (Bibl.110), who have reported that an equilibrium mixture containing all 5 possible tetraalkylsilanes
is formed when approximately equimolecular quantities of tetraethylsilane and tetra-
propylsilane are boiled 5 hours at 175-180°C in the presence of 2.5 mol-% of AlCl₃. Processes leading to the thermal rearrangement of chlorobromosilanes and chloroiodo-
silanes at 600°C without a catalyst are also known. In the presence of aluminum chloride, partial rearrangement may be accomplished on heating halosilanes 7 hours at 140°C. The replacement of the hydrogen by chlorine has been observed in synthesis of chlorosilanes from silanes and dichlorosilanes.

When various methylchlorosilanes are heated at 150°C in an autoclave in the presence of inorganic chlorides as catalysts, there is an exchange reaction of the hydrocarbon radical attached to the silicon atom (Bibl.III).

The process may be conducted in a sealed autoclave at temperatures from 250 to 150°C and pressures ranging respectively from 30 to 100 atm (a load of about 2.3 mols to the liter of reaction volume of the autoclave). Aluminum chloride, in an amount of about 2%, is the best catalyst, but at a temperature about 400°C, the reaction also proceeds well even without a catalyst.

When trimethylchlorosilane is heated 15 hours at 300°C under a pressure of 54 atm in the presence of 2.3% of aluminum chloride, a mixture containing 7.8% of tetramethylsilane, 76.4% of trimethylchlorosilane, and 9.1% of dimethyldichlorosilane is formed. Considering that the equilibrium is attained under the conditions of the reaction, the equilibrium constant for the reaction

\[ 2(CH₃)₃SiCl \rightleftharpoons (CH₃)₃Si + (CH₃)₃SiCl₂ \]

may be calculated for the temperature of 300°C:

\[ K_{300} = \frac{(0.764)^2}{0.078 \cdot 0.91} = 82.5 \]

With increasing temperature, the equilibrium is somewhat shifted to the right (\( K_{3500} = 74.3; K_{4200} = 54.9 \)). At 450°C, in the absence of a catalyst, equilibrium
is reached after 7 hours (at 108 atm). In the equilibrium state, the reaction mixture contains 7.4% of tetramethylsilane, 75.7% of trimethylchlorosilane, and 11% of dimethyldichlorosilane (K = 66).

When dimethyldichlorosilane is heated 7 hours at 300°C under pressure of 47 atm in the presence of 2% of aluminum chloride, a mixture containing 7.6% of trimethylchlorosilane and 12% of methyltrichlorosilane is formed. Equilibrium is obviously not reached, since from an equimolecular mixture of trimethylchlorosilane and methyltrichlorosilane under similar conditions a mixture containing 15% of trimethylchlorosilane and 21% of methyltrichlorosilane is obtained. When thermal rearrangement of either dimethyldichlorosilane or a mixture of methyltrichlorosilane and trimethylchlorosilane in various ratios is run at 350°C, equilibrium can be reached, and the reaction constant:

\[ 2(CH_3)_2SiCl_2 \rightleftharpoons (CH_3)_3SiCl + CH_3SiCl_3 \]

amounts to \( K_{350°C} = 39.9 \) (with very insignificant deviation in the individual experiments). Neither SiCl₄ nor tetramethylsilane are detected in the reaction products.

On the thermal rearrangement of methyldichlorosilane by the reaction

\[ 2CH_3SiCl_3 \rightleftharpoons (CH_3)_3SiCl + SiCl_4 \]
equilibrium cannot be attained. At 150°C under 64 atm pressure for 7 hours, in the presence of 2.1% of aluminum chloride, a mixture is formed, containing only 3.1% of dimethyldichlorosilane, together with 94% of methyltrichlorosilane and traces of SiCl₄, while, under similar conditions, an equimolecular mixture of dimethyldichlorosilane and SiCl₄ yields 31% of dimethyldichlorosilane, 24.3% of methyltrichlorosilane and 44.9% of SiCl₄. When aluminum chloride is used, it has also not been possible to reach equilibrium: at 450°C under pressure of 100 atm, methyltrichlorosilane, with 1.7% of aluminum chloride, gives 2.8% of dimethyldichlorosilane, 66% of methyltrichlorosilane, and 11.4% of SiCl₄, while an equimolecular mixture of dimethyldichloro-
Silane and \( \text{SiCl}_4 \) under these conditions gives 9.8% of dimethyldichlorosilane, 50% of methyltrichlorosilane, and 20.6% of silicon tetrachloride. The low reaction velocity is obviously due to the considerable value of the reactivation energy.

A mixture of 2 mols of \( \text{SiCl}_4 \) and 1 mol of trimethylchlorosilane at 375°C, in the presence of 1.8% of aluminum chloride, shows practically no change in its composition; a mixture of methyltrichlorosilane and dimethyldichlorosilane likewise almost fails to react. From a mixture of equimolecular quantities of tetramethysilane and \( \text{SiCl}_4 \), when heated 13 hours at 290-325°C, in the presence of 2% of aluminum chloride, 5% of trimethylchlorosilane and 3% of dimethyldichlorosilane is obtained, while no methyltrichlorosilane is formed.

When methylchlorosilane is heated to 325°C (83 atm) in the presence of 2% of aluminum chloride, the following are formed: 0.6% of gaseous products (HCl, methane, chlorosilane), 1.2% of dichlorosilane, 7.2% of trichlorosilane, 30.7% of methyl dichlorosilane, 29.5% of methyltrichlorosilane, and 17.5% of dimethyldichlorosilane.

In all cases where the process of thermal rearrangement is conducted at 375°C or higher, methane appears in the reaction product, as well as high-boiling chlorosilanes containing the \(-\text{Si-C-Si}\) group. The formation of such compounds is due to the following irreversible side reactions, into which the methylchlorosilanes may inter:

\[
2\text{CH}_3\text{SiCl}_3 \rightarrow \text{CH}_4 + \text{CH}_3\text{SiCH}_2\text{SiCl}_3
\]
\[
2(\text{CH}_3)_2\text{SiCl} \rightarrow \text{CH}_4 + \text{CH}(_2)\text{SiCH}_3\text{SiCH}_3\text{SiCH}_3\text{SiCH}_3\text{SiCl}\]

The equilibrium constants of the reaction of disproportionation of methylchlorosilanes have been determined (Bibl.112).

**Method of Determination and Apparatus.** Weighed amounts of chlorosilanes and the catalysts (aluminum chloride) are placed in a bomb. This bomb is connected by means of two cocks with an intermediate receiver, and then with bulbs for taking...
samples. After the bomb has been charged, the cocks are closed, the air is pumped out of the intermediate receiver, and the bomb is heated 15-20 hours. During the process of heating, samples are taken and analyzed on the mass spectrometer, which has previously been calibrated for various mixtures of methylchlorosilanes.

If, to save space, the substances and their concentrations are denoted by the following symbols:

\[
\begin{align*}
\text{SiCl}_4 &= Q \\
\text{CH}_3\text{SiCl}_3 &= T \\
\text{(CH}_3\text{)SiCl}_2 &= D \\
\text{(CH}_3\text{)SiCl} &= S
\end{align*}
\]

then the equilibrium constant for the system MDT at 350°C under pressure of 17.3 kg/cm² is:

\[
K = \frac{D^2}{M \cdot T} = 91.9
\]

The thermodynamic characteristics of the reactions in the systems SMD and MDT are as follows:

<table>
<thead>
<tr>
<th>System</th>
<th>SMD</th>
<th>MDT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibrium Constant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 350°C</td>
<td>74.3</td>
<td>39.3</td>
</tr>
<tr>
<td>at 420°C</td>
<td>59.9</td>
<td>29.8</td>
</tr>
<tr>
<td>Thermal Effect of Reaction, kcal</td>
<td>-3.6</td>
<td>-3.6</td>
</tr>
<tr>
<td>Free Energy, kcal</td>
<td>5.4</td>
<td>-4.7</td>
</tr>
<tr>
<td>Entropy, in Entropy Units</td>
<td>2.8</td>
<td>1.6</td>
</tr>
</tbody>
</table>

In the system DTQ the velocity of reaction is very low. Thus, for instance, pure CH₃SiCl₃(T) at 420°C in the presence of 5 g of aluminum chloride after 20 hours was only 8% rearranged. The composition of the mixture after 20 hours was as follows: D = 4.3%, T = 92% and Q = 1.4%.
At the same time, a mixture of equivalent quantities of D and Q under these same conditions showed only 10% of T after 20 hours, and consisted of 45% each of D and Q. This slow pace of the reaction probably depends on its high energy of activation.

The kinetics of the reaction have been studied mainly on the system MDT. To determine whether the reaction is of homogeneous or heterogeneous character, 11 g of fine steel wire, coiled into a lump and having a surface of 200 cm² for each gram of the reacting substances, was placed in a reaction bomb. Since, in spite of the tenfold increase in the surface area, the velocity of the reaction remained practically the same, it may be concluded that the reaction is of homogeneous character.

It must also be noted that at a temperature of 350°C, the methylchlorosilanes can exist only in the form of gases, since their critical temperatures lie below the temperature of the experiment. The critical temperature of aluminum chloride is 357°C. Thus the greater part of the aluminum chloride should also consist of gas.

It has been found that the time required for the reaction to pass from 25% to 50% of completion amounts to 1/3 of the time necessary to reach the equilibrium state. If we denote this period by \( t_{1/3} \), we may note that the function \( \frac{1}{t_{1/3} [\text{AlCl}_3]} \) practically does not change with the concentration of aluminum chloride, and is constant under the given conditions.

In turn, the relation between \( t_{1/3} \) and \( [\text{AlCl}_3] \) is expressed by a straight line. Since the expression \( \frac{1}{t_{1/3}} \) is proportional to the rate of reaction, the rate of reaction is proportional to the quantity of aluminum chloride.

The value of \( t_{1/3} \) does not depend on the initial concentration of the reagents, for a constant concentration of aluminum chloride. The disproportionation reaction is a first-order reaction.

It is interesting to note the following experiment.

In a bomb, 53.4 g of dimethylchlorosilane was placed. The apparatus was heated to 350°C, and the pressure in it amounted to 48 atm. Then 460 g of aluminum
chloride was added to the bomb and it was again heated to 350°C. The pressure in the apparatus was 48.4 atm, while the theoretically calculated increase of pressure due to the aluminum chloride should have been not 0.4 atm, but 5.4 atm. This experiment speaks for the view that the aluminum chloride almost completely forms complex compounds with the methylchlorosilanes.

The most probable mechanism for the disproportionation reaction is as follows:

\[
\begin{align*}
(CH_3)_2SiCl_2 + AlCl_3 &\longrightarrow (CH_3)_2SiCl_2\cdot AlCl_3 \\
(CH_3)_2SiCl_2 + (CH_3)_2SiCl_2\cdot AlCl_3 &\rightleftharpoons (CH_3)_2SiCl + (CH_3)_2SiCl_3 \cdot AlCl_3 \\
CH_3SiCl_2 \cdot AlCl_3 + (CH_3)_2SiCl_2 &\rightleftharpoons CH_3SiCl_3 + (CH_3)_2SiCl_3 \cdot AlCl_3
\end{align*}
\]

Reaction (1) proceeds many times faster than reactions (2) and (3). Reaction (3), in turn, is faster than reaction (2).

The following data is presented on the rate of reaction (2) in the forward and reverse direction:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate of Forward Reaction</th>
<th>Rate of Reverse Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>at 350°C</td>
<td>$4.1 \times 10^{-5}$</td>
<td>$2.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>at 375°C</td>
<td>$7.3 \times 10^{-5}$</td>
<td>$4.93 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

The value of K is expressed by the ratio between the velocity of the forward reaction and the velocity of the reverse reaction:

\[ K = \frac{v_{\text{forward}}}{v_{\text{reverse}}} \]

Values of the Reaction Constants

<table>
<thead>
<tr>
<th>Constant of Reaction (2)</th>
<th>at 350°C</th>
<th>at 375°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.116</td>
<td>0.117</td>
<td></td>
</tr>
<tr>
<td>Constant of Reaction (3)</td>
<td>0.171</td>
<td>0.174</td>
</tr>
</tbody>
</table>

On the basis of these data the value of the activation energy of reaction (2)
can be approximately calculated. It is about 22 kcal.

The mechanism of the process is probably as follows: the aluminum chloride adds to a chlorine atom of dimethyldichlorosilane, thus weakening the Si-Cl bond. The further course of the process is connected with the dissociation of the complexes so formed into a positive dialkylchlorosilane ion and tetrachloroaluminate ion, as is postulated in the Friedel-Crafts reactions:

\[
(CH_3)_2SiCl_2·AlCl_3 \rightleftharpoons [(CH_3)_2SiCl]_+ + [AlCl_4]^- 
\]

It must be assumed that the rearrangement takes place owing to the weakening of the Si-C and Si-Cl bonds as a result of the addition of the aluminum chloride to the molecule of the corresponding methyldichlorosilane.

The most varied alkyl- and arylchlorosilanes may enter into the reaction of thermal rearrangement. Thus, for example, when 1.38 mol of diphenyldichlorosilane is heated with 1.25 mol of SiCl₄ in a copper-lined steel autoclave at 350°C, under a pressure of 32 atm, in the presence of 0.8% aluminum chloride, for 4 hours, 1 mol of phenyltrichlorosilane is formed and, in addition, 0.7 mol of benzene.

1.87 mol of phenyltrichlorosilane and 1.9 mol of trimethylchlorosilane, heated in the presence of 0.8% of aluminum chloride at 325°C for 4 hours, yield 0.33 mol of phenylmethyldichlorosilane.

Since it is impossible to separate phenyltrichlorosilane from phenylmethyldichlorosilane by rectification, owing to the proximity of the boiling points, 200°C and 204°C, the composition of the mixture is determined by esterification of the chlorides by ethanol, followed by fluorination and separation of the phenylmethyldichlorofluorosilane by rectification.

A mixture of 1 mol of phenyltrichlorosilane and 2.01 mols of trimethyldichlorosilane, heated 4 hours in the presence of 2% of aluminum chloride at 350°C, under 57 atm pressure, yields 0.18 mol of phenylmethyldichlorosilane.

Heating a mixture of 1.54 mol of ethyldichlorosilane and 1.53 mol of dimethyl-
dichlorosilane in the presence of 2% aluminum chloride at 375°C for 5 hours gives 0.2 mol of dimethylethylidichlorosilane. The product may be separated from the reaction mixture by esterification of the mixture with absolute ethanol, followed by rectification. A mixture of equimolecular quantities of diphenyldichlorosilane and SiCl₄, at 350°C, either in the presence of aluminum chloride or in its absence, yields a certain amount of phenyltrichlorosilane, but this compound is formed not as a result of a disproportionation reaction, but by the reaction of diphenyldichlorosilane with HCl:

$\text{(C}_6\text{H}_5\text{)}_2\text{SiCl}_2 + \text{HCl} \rightarrow \text{C}_6\text{H}_5\text{SiCl}_3 + \text{C}_6\text{H}_6$

since benzene is always formed in amounts roughly equivalent to the phenyltrichlorosilane.

**Method of Conducting the Disproportionation Reaction of Alkyl-(Aryl)-Chlorosilanes.**

1. In a copper lined 1.30 liter autoclave, 386 g (1.52 mol) of diphenyldichlorosilane and 258 g (1.51 mol) of SiCl₄ (40% by weight) are placed. The temperature of the mixture is slowly raised over a 3 hour period of 350°C (35 atm), and the mixture is held at 1 hour at this temperature. The temperature is then raised to 375°C, and after holding the mixture 2 hours at this temperature, the autoclave is cooled. Rectification of 515 g of liquid reaction mass yields 187 g of SiCl₄, which amounts to 91% of the quantity taken in the reaction, as well as about 4 g of benzene and 7.4 g of phenyltrichlorosilane, of the boiling point 194-202°C.

2. In an autoclave not lined with copper 1.3 liter in capacity 350 g (1.38 mol) of diphenyldichlorosilane, 213 g (1.25 mol) of SiCl₄, and 4 g of anhydrous aluminum chloride are placed, and the mixture is heated 4 hours at 350°C and 32 atm pressure. The liquid reaction mixture is then distilled, yielding 213.2 g (1.01 mol) of phenyltrichlorosilane, boiling point 197-200°C, and 54.2 g (0.7 mol) of benzene.

3. In a 3.4 liter autoclave, 396 g or 1.87 mol of phenyltrichlorosilane, 207 g or 1.90 mol of trimethylchlorosilane, and 5.0 g or 0.037 mol of anhydrous aluminum
chloride are placed. After heating 4 hours at 325°C, trimethylchlorosilane, dimethylchlorosilane, methyltrichlorosilane, and benzene are distilled from the liquid reaction mass up to 175°C. Fractionation of the residue over sodium chloride yields 102 g of liquid of the boiling point 190-205°C, containing 40.6% of chlorine. Methylphenyldichlorosilane was detected in the product and was separated by converting into methylphenyldiethoxysilane (51 g), boiling point 221.5-223°C. A similar product was prepared from methyldichlorosilane and anhydrous ethanol. It passed over at 221.5°C, while phenyltriethoxysilane boils at 235-237°C. The 51 g of methylphenyldiethoxysilane was then treated with anhydrous HF. The methyldifluorosilane so formed was extracted with pentane and fractionated, yielding 23.2 g of a product with the boiling point 141.2-141.7°C. The boiling point of methylphenyldifluorosilane is 142-142.5°C. The fluoride-ion content by analysis (titration in the presence of calcium chloride) was 23.8% and 23.5%. The theoretical content would be 24.0%. 

4. In a 1.3 liter autoclave, 212.5 g or 1.00 mol of phenyltrichlorosilane, 259 g, or 2.01 mol of dimethylchlorosilane, and 10 g of aluminum chloride are placed. The autoclave is heated 4 hours at 35°C (57 atm). The reaction mixture is treated as in the preceding case, yielding about 29 g or 0.18 mol of methylphenyldifluorosilane, with the boiling point 141-142°C.

5. In a 3 liter autoclave, 198.5 g, or 1.54 mol, of dimethyldichlorosilane, 249.1 g or 1.53 mol of ethyltrichlorosilane, (boiling point 100°C), and 10 g of aluminum chloride are placed. After heating 5 hours at 375°C, the mixture is treated as indicated in paragraph "c", yielding 130 g of a mixture of ethylchlorosilane and methylethylidichlorosilane, boiling point 100.5°C. The mixture, containing 57.7-57.8% of chlorine, was treated with absolute ethanol, yielding 32.8 g of methylethylidioethoxysilane. The principal fraction (14.3 g), boiling at 140°C, has a refraction index nD = 1.3590.
Reaction with Aluminum Chloride

The cleavage of the organic radicals in alkyl-(aryl)-chlorosilanes may take place under the action of aluminum chloride. Diphenyldichlorosilane and ethyl bromide in the presence of aluminum chloride, actively react, even at room temperature, by the reaction:

\[
\begin{align*}
(\text{C}_6\text{H}_5)_2\text{SiCl}_2 + \text{AlCl}_3 \rightarrow & \text{C}_6\text{H}_5\text{H}_2 + \text{C}_6\text{H}_5\text{SiCl}_3 + \text{AlCl}_3\text{Br} \\
\text{C}_6\text{H}_5\text{SiCl}_3 + \text{AlCl}_3 + \text{C}_2\text{H}_4\text{Br} \rightarrow & \text{C}_6\text{H}_5\text{H}_2 + \text{SiCl}_4 + \text{AlCl}_3\text{Br}
\end{align*}
\]

In the absence of ethyl bromide, diphenyldichlorosilane reacts with aluminum chloride when heated to 70°C:

\[
(\text{C}_6\text{H}_5)_2\text{SiCl}_2 + \text{AlCl}_3 \rightarrow \text{C}_6\text{H}_5\text{H}_2\text{AlCl}_2 + \text{C}_6\text{H}_5\text{SiCl}_3
\]

A Few Specific Reactions of Alkyl-(Aryl)-Fluorosilanes and Iodosilanes

The alkyl-(aryl)-fluorosilanes (Bibl.65), are somewhat less active chemically than the alkyl-(aryl)-chlorosilanes, and enter with greater difficulty into most chemical reactions. Thus, for instance, the process of hydrolysis of alkylfluorosilane takes place with considerably less intensity. The reaction of hydrolysis of alkyl-(aryl)-fluorosilanes:

\[
\text{R}_x\text{SiF}_{4-x} + (4-x)\text{H}_2\text{O} \rightleftharpoons \text{R}_x\text{Si(OH)}_{1-x} + (4-x)\text{HF}
\]

is reversible, and proceeds to completion only when a considerable excess of water is used. While alkyltrifluorosilanes, like the chlorosilanes, fume in air, the dialkyldifluorosilanes are already more stable. They do not fume in air, and are only slowly hydrolyzed under the action of water (for instance the hydrolysis of diethyldifluorosilane with an excess of water is completed only after 12 hours). The trialkylfluorosilane, except for trimethylfluorosilane, do not react with cold
water, while the higher trialkylfluorosilanes do not react even with aqueous alkali.
The sharp increase in the stability of the alkylfluorosilanes with increasing number of hydrocarbon radicals is obviously connected not only with the steric factor, but also with the electronic structure of the molecule.

The alkylfluorosilanes are distinguished by exceptional thermal stability. Di-butyldifluorosilane is stable on heating in a sealed tube at 300°C, while the decomposition temperature of trimethylfluorosilane is over 600°C.

The reaction of esterification of alkylfluorosilanes takes place with considerably more difficulty than that of the corresponding alkylchlorosilanes. Thus, for example, the reaction between butylfluorosilanes and methanol can be carried to completion, but with butanol even butyltrifluorosilane reacts slowly and incompletely, and in the initial stage simply dissolves without evolving HF.

The reaction between alkylfluorosilanes and sodium alcoholate proceeds somewhat better. In this case, diisopropyldifluorosilane gives diisopropyldisthoxysilane in 45% yield.

The alkylfluorosilanes have an irritant effect on the organism; propyltrifluorosilane, and particularly n-butyltrifluorosilane, are powerful poisons.

In contrast to hydrogen fluoride, the alkyltrifluorosilanes do not form complex compounds with sodium fluoride, and therefore when alkylfluorosilanes contaminated with HF are passed through tablets of sodium fluoride, a product free from traces of HF may be obtained.

The iodo-derivatives are distinguished from all other alkylhalosilanes by their minimum stability (Bibl.67). The products obtained on rectification in the form of colorless liquids rapidly acquire a dark color in the light, owing to the liberation of small amounts of iodine. The addition of glass wool accelerates the process of decomposition and leads immediately to a considerable darkening of the product.

The alkyliodosilanes, like the alkylchlorosilanes, are hydrolyzed very readily by the action of water, forming hydroxides of the silanes and polysiloxanes. The
reaction with an alcohol leads to the formation of substituted esters. When a mixture of ethyl alcohol and piperidine is added to isopropylidiodosilane, disopropyl-diethoxy-silane in 53% yield is obtained. We recall that under the action of ethyl alcohol on silicon tetraiodide, only ethyl iodide and silica gel is formed.

The iodine atom can be easily replaced by an organic radical under the action of an organomagnesium compound. Under the action of silver cyanide, alkylcyanosilanes are formed:

\[
(C_3H_7)J + AgCN \rightarrow (C_3H_7)JCN + AgJ
\]

It has not been possible to conduct the analogous reaction with tripropylchlorosilane.

'Haloalkyl-(Haloaryl)-Halosilanes

Methods of Preparation

Under the action of halogens on organosilicon compounds, two reactions may occur.

1. Cleavage of the alkyl or aryl radical and its replacement by a halogen, such as, for example, in the bromination of tetraphenylsilane (Bibl.113):

\[
(C_6H_5)J + Br_2 + (C_6H_5)JBr + C_6H_5Br
\]

or on the halogenation of a trialkylhalosilane (Bibl.118):

\[
(Alk)_3SiX + X_2 \rightarrow (Alk)_3SiXX_2 + AlkX
\]

The velocity of this reaction increases in the series \( X = Br < Cl < F < I \).

2. Halogenation of alkyl and aryl radicals of the organosilicon compound, as, for instance, in the chlorination of triethylphenylsilane (Bibl.114):

\[
(C_3H_7)J + Cl_2 \rightarrow (C_3H_7)JCl + H_2
\]
This direction of the reaction is of very great importance. In practice, the two reactions often take place simultaneously. The dominant direction of the reaction depends on the conditions under which the process is conducted and on the presence of catalysts.

As shown by Yakubovich and Ginzburg (Bibl.193), the chlorination of the aromatic nuclei of phenylchlorosilanes is facilitated in the presence of the usual chlorination catalysts (metallic iron, iodine, phosphorus pentachloride, antimony trichloride aluminum chloride), and under ultraviolet irradiation.

It has been found that on the chlorination of phenylchlorosilanes in the presence of such catalysts as compounds of aluminum, of iron, or of antimony, the chlorination is accompanied by a process involving the cleavage of the reaction product at the Si–C bond. When aluminum chloride is used as a catalyst, this cleavage already takes place at the initial stage of chlorination, at temperatures of the order of 50–70°C; in the presence of ferric chloride it takes place only under deep chlorination and at a higher temperature (110–150°C), and at that, only to very insignificant degree. In the presence of antimony trichloride, the chlorination proceeds smoothly and goes to completion without signs of cleavage even of the products of deep chlorination.

The cleavage products of phenyltrichlorosilane and of its chlorine derivatives, on chlorination in the presence of aluminum chloride or of ferric chloride, are chlorophenylchlorosilanes, SiCl₄, and chlorine derivatives of benzene of various degrees of substitution.

The cleavage of the reaction products at the Si–C bond takes place even more in the chlorination of diphenylchlorosilane than on the chlorination of phenyltrichlorosilane. Thus, when aluminum chloride or ferrous chloride is used as a catalyst, the cleavage of the reaction product takes place already at the temperature of 30°C, at the very beginning of chlorination. In the presence of antimony trichloride, this process is observed on deeper chlorination, and at higher temperatures.
The chlorination of diphenyldichlorosilane in the presence of iron or antimony compounds, at temperatures of 70-120°C, leads to the formation of a complex mixture of chlorine derivatives of diphenyldichlorosilanes and of phenyltrichlorosilanes and of chlorine derivatives of benzene of various degrees of substitution.

According to data of Rochow (Bibl.115), the chlorination of diphenyldichlorosilane under these conditions leads to the formation only of chlorine derivatives of diphenyldichlorosilane which is not in agreement with the data of other investigators.

The chlorination of phenylchlorosilane in the presence of iodine and phosphorus pentachloride takes place at a temperature of 110-110°C without cleavage of the chlorination product, but these catalysts only weakly catalyze the chlorination process. Iodine and phosphorus pentachloride may be used to prepare monochloro-derivatives of phenyltrichlorosilane and triphenyldichlorosilane.

Chlorination at 100°C and over, without catalysts, or chlorination under ultraviolet irradiation of the reaction mixture at 70°C, does not lead to the cleavage of the Si-C bond in phenyltrichlorosilane and diphenyldichlorosilane.

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The cleavage of the Si-C bond in the presence of catalysts increases with the chlorination temperature; it may be minimized by conducting the chlorination under milder conditions (for instance at a temperature of 20-30°C in a medium of carbon tetrachloride or some other solvent inert with respect to chlorine). The cleavage of phenyltrichlorosilane and of diphenyltrichlorosilane in the presence of the chlorides of iron, aluminum, or antimony, increases as the chlorine atoms accumulate in the phenyl nuclei of these compounds. The process of cleavage may lead to formation of SiCl₄, on the one hand, and of organometallic compounds, on the other.

The formation of organometallic compounds is confirmed by the separation of chlorophenylantimony dichloride from the reaction products.

On the basis of these data, the process of cleavage of phenylchlorosilanes on their chlorination in the presence of aluminum chloride, ferric chloride, or antimony trichloride, may be represented by the following general formula:
Consequently, the principal cause of the cleavage of phenylchlorosilanes on their chlorination in the presence of ferric chloride, aluminum chloride, or of antimony trichloride, is the formation of organic compounds of these metals, which are then immediately broken down under the action of chlorine; thus regenerating MeCl$_3$, which then leads to further cleavage of the phenylchlorosilanes.

The chlorination of phenylchlorosilane in the presence of aluminum chloride is very intense, and proceeds with great liberation of heat, leading to the resinification of the reaction product.

In the presence of antimony trichloride, the side process of cleavage of the phenyltrichlorosilanes and the products of its chlorination is observed to a considerably lesser degree than in the presence of aluminum chloride, even at elevated temperatures. For this reason, chlorination in the presence of antimony trichloride makes it possible to prepare polychloro-derivatives of phenylchlorosilanes in rather good yield, up to 90%, in the chlorination of phenyltrichlorosilane, and up to 65% in the case of the chlorination of diphenyldichlorosilane. In this way, chlorine derivatives of phenyltrichlorosilane, from the monochloro- to the di- and trichloro-phenyltrichlorosilane has been prepared. The preparation of the chlorine derivatives of diphenyldichlorosilane of a higher degree of chlorination involves great difficulties, in view of the fact that the cleavage of the -Si-C- bond increases markedly with the temperature. Such constituents in the nucleus as the -SiCl$_3$ group and the SiCl$_2$ group, by their nature, should orient the chlorine into the meta-position, that is, hinder the course of the substitution reactions in the benzene ring. This is in fact confirmed by the fact that the reaction of chlorination of phenyltri-
chlorosilane (in the meta-position) proceeds only poorly, and that this substance is chlorinated only with difficulty in the absence of catalysts.

The chlorination of phenyltrichlorosilanes in the presence of the usual catalysts proceeds readily, and the orientation is modified in this case, that is, the $\text{-SiCl}_3$ group proves to be a para- and ortho-orienting substituent.

The chlorination of arylichlorosilanes is most easily accomplished under the action of elementary chlorine at a temperature of $70-120^\circ\text{C}$ in the presence of catalysts: antimony trichloride, or of ferric chloride (in an amount equal to 0.5% of the weight of the arylichlorosilanes), or of antimony pentachloride (0.1%). Thus, on the chlorination of diphenyldichlorosilane (Bibl.116) in the presence of 0.1% of antimony pentachloride at 70-80$^\circ\text{C}$, the process proceeds with the liberation of a considerable amount of heat. The principal reaction product is di-(trichlorophenyl)-dichlorosilane:

$$\text{(C}_6\text{H}_5)_2\text{SiCl}_2 + 6\text{Cl}_2 \rightarrow \text{(C}_6\text{H}_5)_2\text{SiCl}_4 + 6\text{HCl}$$

By further chlorination at 120$^\circ\text{C}$, di(pentachlorophenyl)-dichlorosilane may be obtained:

$$\text{(C}_6\text{H}_5)_2\text{SiCl}_2 + 4\text{Cl}_2 \rightarrow \text{(C}_6\text{H}_5)_2\text{SiCl}_6 + 4\text{HCl}$$

The reaction of chlorination of benzylichlorosilanes may be accomplished by sulfuryl chloride in the presence of benzoyl peroxide.

On the action of halogens on tetraalkylsilanes, without heating (chlorine) or with slight heating (bromine), tetraalkylsilanes containing a halogen atom in the radical are obtained. Usually in this case mixtures of haloalkylsilanes are formed. This was shown by Friedel and Crafts (Bibl.137) who obtained a mixture of mono- and dichloro-derivatives of tetraethylsilanes by the chlorination of tetraethylsilane. They established by this example that organosilicon compounds may be chlorinated without breaking the Si-C bond.
As shown by Ushakov and Itenberg (Bibl.117) the chlorination of \((\text{C}_2\text{H}_5)\text{LSi}\) proceeds more readily in the presence of 1-2% of phosphorus pentachloride. Under these conditions, two monochlorides are formed, the \(\alpha\)- and \(\beta\)-chloroethyldiethylsilanes.

The velocity of these reactions is also appreciably increased under ultraviolet irradiation (Bibl.118). On the photochemical chlorination of methylchlorosilanes, a mixture of chloromethylchlorosilanes of various degrees of chlorination is formed (Bibl.119). The vapor-phase chlorination of dimethylchlorosilanes by chlorine has been accomplished, yielding mainly chloromethylmethyldichlorosilane (Bibl.120).

It has been found that on the chlorination of alkylsilanes by elementary chlorine, the halogen enters for the most part at an already halogenated carbon atom, and when methyl radicals are present, trichloromethylsilanes are mainly formed.

A study of the products of the chlorination of trimethylchlorosilane and dimethylchlorosilane has established that the chloromethyl group is more readily chlorinated than an unsubstituted methyl group (Bibl.121).

Sulfuryl chloride, in the presence of benzoyl peroxide, is an excellent chlorinating agent in alkyltrichlorosilanes (Bibl.122). When it is used, process conditions may be selected so as to obtain, for instance, on the chlorination of ethyltrichlorosilane, almost exclusively \(\alpha\)-chloroethyltrichlorosilane in 90% yield, while when this reaction is conducted under ordinary conditions, \(\beta\)-chloroethyltrichlorosilane is the principal product. It is interesting to note that the methyl group of methyltrichlorosilane is not chlorinated by sulfuryl chloride.

When sulfuryl chloride is used to chlorinate alkylchlorosilanes with longer aliphatic radicals, such as, for instance, propyltrichlorosilane, a mixture of \(\alpha\), \(\beta\), \(\gamma\)-derivatives is obtained, and it has been found that the replacement of the hydrogen atom by a chlorine atom at the \(\alpha\)-carbon atom takes place with somewhat greater difficulty than at the \(\beta\)-carbon atom; the hydrogen atom at the \(\alpha\)-carbon is replaced by chlorine with still greater difficulty, owing to the proximity (Bibl.123) of the \(-\text{SiCl}_3\) group. The proportions of the compounds formed are \(\alpha:\beta:\gamma = 1:3.5:3.1\).
On the chlorination of trialkylchlorosilane by sulfuryl chloride in the presence of benzoyl peroxide, their monochloro-derivatives may be obtained in good yield; thus, on the chlorination of \((\text{C}_2\text{H}_5)\text{SiCl}\) a mixture containing \(\alpha\)- and \(\beta\)-chloroethylidichlorosilanes is obtained (Bibl.124).

The chlorination of the alkylchlorosilanes by the action of sulfuryl chloride in the presence of benzoyl peroxide is more convenient than with chlorine, since the process can be more easily controlled. We present a few techniques of conducting the chlorination reaction by various methods (Bibl.125).

**Chlorination of Alkylchlorosilanes by Chlorine.**

1. In a reaction flask provided with a reflux condenser, a mixer, and a tube for introducing chlorine under the liquid layer, 130 g (0.87 mol) of methyltrichlorosilane is placed (Bibl.126). The condenser is cooled by brine and is connected with the atmosphere through a trap chilled by a mixture of solid carbon dioxide and acetone. The reaction flask is irradiated by a 460 watt sun-lamp placed at a distance of half a meter. The chlorine enters from a cylinder through a drier under the layer of methylchlorosilane, and the \(\text{HCl}\) is removed through the reflux condenser and the trap. The process of chlorination is conducted at the boiling point of the mixture, which gradually rises from 66°C to 150°C. Rectification of the mixture yields 121 g of trichloromethyltrichlorosilane, with the boiling point 155-156°C (740 mm), in white waxy crystals with the melting point 114-116°C. The yield is 55% of the theoretical.

2. In the apparatus of N.I.Kursanov, 1100 g, or 8.5 mols, of dimethyldichlorosilane are heated to boiling (70°C). When the dimethyldichlorosilane vapor has filled the upper globe of the apparatus, chlorine is supplied at a rate such that the temperature in the globe does not rise above 110°C. The bubbler is closed by a copper mesh, and the globe of the apparatus is irradiated by a mercury lamp. The reaction is completed at the boiling point of the products in the lower part of the apparatus, (124°C). The yield is 61% of chloromethylmethyldichlorosilane.

Under similar conditions (Bibl.127) a mixture of the following composition was
obtained:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Yield %</th>
<th>Boiling Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyldichlorosilane</td>
<td>25.9</td>
<td>70.10</td>
</tr>
<tr>
<td>Methylchloromethyldichlorosilane</td>
<td>25.7</td>
<td>121.30</td>
</tr>
<tr>
<td>Di-(chloromethyl)-dichlorosilane</td>
<td></td>
<td>107.2-107.80</td>
</tr>
<tr>
<td>Methyl-(dichloromethyl)-dichlorosilane</td>
<td>32.5</td>
<td>100.50 (150mm)</td>
</tr>
<tr>
<td>Methyl-(trichloromethyl)-dichlorosilane</td>
<td>6.4</td>
<td>1090 (151mm)</td>
</tr>
</tbody>
</table>

3. Into 1085 g of trimethylchlorosilane, under ultraviolet irradiation, dried chlorine is passed until the weight increase of the reaction mixture reaches 366 g. Rectification of the reaction product in a column with 20 theoretical plates, yields the following substances:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Yield %</th>
<th>Boiling, 0C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trimethylchlorosilane (unreacted)</td>
<td>18.9</td>
<td></td>
</tr>
<tr>
<td>Dimethyldichloromethylchlorosilane</td>
<td>15.5</td>
<td>115-115.5</td>
</tr>
<tr>
<td>Dimethyldichloromethylchlorosilane</td>
<td>20.7</td>
<td>149.1-149.9</td>
</tr>
<tr>
<td>Methyl-bis(chloromethyl)chlorosilane</td>
<td>7.65</td>
<td>171.1-172.8</td>
</tr>
<tr>
<td>High-Boiling Products</td>
<td>7.35</td>
<td></td>
</tr>
</tbody>
</table>

Such a composition of the mixture argues for the view that the chloromethyl group at the silicon atom is chlorinated more easily than the methyl group. On chlorination of trimethylchlorosilane and dimethyldichlorosilane, flashes are often observed, which is particularly the case on rapid feeding of the chlorine and ultraviolet irradiation.

Chlorination of Alkylchlorosilanes by Sulfuryl Chloride. 1. A solution of 100 g of trimethylchlorosilane (Bibl.128), 124 g of sulfuryl chloride, and 0.5 g of benzoyl peroxide in 200 ml of chlorobenzene is heated 3 hours under a reflux con-
The reaction product is dimethylchloromethylchlorosilane \((\text{CH}_3)_2(\text{CH}_2\text{Cl})\text{SiCl}_3\), in 38% yield. If sulfuryl chloride, in the same proportions, is introduced into a heated mixture of trimethylchlorosilane, chlorobenzene, and benzoyl peroxide, then the yield will amount to 52%, and an insignificant amount of dimethyldichlorosilane will be formed as a by product.

2. A mixture of 1300 g of ethyltrichlorosilane and 1070 g of sulfuryl chloride (Bibl.129), is boiled in the presence of benzoyl peroxide, forming a mixture of the following product: ethyltrichlorosilane, 440 g, boiling point 100°C (760 mm); \(\alpha\)-chloroethyltrichlorosilane, 216 g, boiling point 138°C (734 mm); and \(\beta\)-chloroethyltrichlorosilane, 550 g, boiling point 152°C (734 mm). In the absence of an organic peroxide, sulfuryl chloride does not chlorinate ethyltrichlorosilane.

3. A mixture of 411 g (2.7 mol) of triethylchlorosilane, 297 g (2.2 mol) of sulfuryl chloride, and 1 g of benzoyl peroxide (Bibl.79), is heated 4 hours under a reflux condenser. The reaction product contains: triethylchlorosilane, 183 g; \(\alpha\)-chloroethyldiethylchlorosilane, 99.5 g, boiling point 110°C (110); and 72.5 g of \(\beta\)-chloroethyldiethylchlorosilane, \(\text{ClCH}_2\text{CH}(\text{C}_2\text{H}_5)_2\text{SiCl}\), boiling point 132°C (100 mm). The total yield of monochloro-derivatives amounts to 60%.

4. Heating of a mixture of 671 g of propyltrichlorosilane (Bibl.130), 546 g of sulfuryl chloride, and 1 g of benzoyl peroxide, under a reflux condenser for 12 hours yields: \(\alpha\)-chloropropyltrichlorosilane, 78 g; \(\beta\)-chloropropyltrichlorosilane, 273 g; \(\gamma\)-chloropropyltrichlorosilane, 242 g (molar ratio 1 : 3.5 : 3.1).

5. Heating of a mixture of 48 g of tert-butyltrichlorosilane (Bibl.120), 36 g of sulfuryl chloride, and 0.5 g of benzoyl peroxide yields 22.6 g of chlorobutyltrichlorosilane (yield 40%). The product consists of crystals with a melting point of 46-47°C and a boiling point of 180°C (739 mm). It has a lacrimatory action.

6. A mixture of 125 g of benzyltrichlorosilane, 54 g of sulfuryl chloride and 1 g of benzoyl peroxide, heated 10 hours, yields 43 g of \(\alpha\)-chlorobenzyltrichlorosilane (Bibl.128), with boiling point 213°C (735 mm), and 162°C (75 mm). Yield 90%.
On chlorination of triethylfluorosilane by sulfur chloride in the presence of benzoyl peroxide, α-chloroethyl-diethylfluorosilane and β-chloroethyl-diethylfluorosilane are obtained. On titration of these compounds against alkali, all the chlorine atoms in the α-position are unaffected, while those in the β-position are almost completely hydrolyzed (98%).

Unsaturated haloalkylhalosilanes can be easily prepared by reacting halo-hydrocarbons of the acetylene series with silanes containing a hydrogen attached to the silicon.

The synthesis of α, β-dichlorovinyltrichlorosilane has been accomplished by the reaction between trichlorosilane and dichloroacetylene (Bibl.131):

\[ \text{HSiCl}_3 + \text{CCI} \equiv \text{CCI} \rightarrow \text{CIHC} \equiv \text{CCISiCl}_3 \]

The authors state that this reaction is accelerated in the presence of a peroxide, on ultraviolet irradiation of the mixture, or on heating it to high temperatures (close to the decomposition temperature of dichloroacetylene).

**Preparation of α, β-Dichlorovinyltrichlorosilane from Trichlorosilane and Dichloroacetylene.** The reaction between trichlorosilane and dichloroacetylene was conducted in a round-bottomed 250-mm flask filled to the neck with tablets of chemically pure caustic soda. The flask was submerged in an oil bath heated to 260°C, and the air was removed from the flask by slow passage of a stream of nitrogen. After about 90 minutes, dropwise introduction of 20 ml of trichloroethylene was commenced from a dropping funnel through a tube running to the bottom of the reaction flask. The dichloroacetylene so formed, contaminated by trichloroethylene and a certain amount of water, was collected in a Claisen flask, submerged in a cooling mixture of ice and salt. To remove the water entering the dichloroacetylene, 3 ml of trichlorosilane was added to it, and then the dichloroacetylene was distilled from the Claisen flask into a Carius tube (with an elongated neck) submerged in a cooling mixture. In order to secure complete distillation of the dichloroacetylene,
the water bath on which it was distilled was gradually warmed to 75°C. After comple-
tion of the distillation, the receiver was closed to prevent the dichloroacetylene
from coming in contact with air, and was removed from the distillation flask. In
taking the apparatus apart there is always a certain danger that the residues of the
dichloroacetylene may explode, and therefore, after removing the admixtures, the dis-
tillation of flask should be dried in a stream of inert gas (preferably nitrogen).

To the dichloroacetylene collected in the carius tube (together with a certain
amount of contaminations, it weighs 7 g), 10 ml of trichlorosilane, containing 0.7 ml
of a 30% of acetyl peroxide in dimethyl phthalate, is added. The tube is sealed and
is then heated 65 hours in a furnace at 70°C. In some cases the tubes explode on
heating, and they must therefore be placed in protective shells.

Distillation of the contents of the tube yields 4.7 g (28%) of \( \alpha, \beta \)-dichloro-
vinyltrichlorosilane; boiling point 87-92°C (55 mm); refractive index \( n^0_{D} = 1.4988 \).

In working with dichloroacetylene, great caution must be used, since it often
explodes, not only in the presence of air, but even in a sealed tube.

\( \alpha, \beta \)-dichlorovinyltrichlorosilane may also be prepared by the reaction between
tetrachloroethane and trichlorosilane:

\[
\text{HCCI}_{3} + \text{CHCl}_{2} + \text{HSiCl}_{4} \rightarrow 2\text{HCl} + \text{CHCl} = \text{CCl}_{3} - \text{SiCl}_{3}
\]

Preparation of \( \alpha, \beta \)-Dichlorovinyltrichlorosilane by the Reaction Between
Tetrachloroethane and Trichlorosilane. A mixture of 26.5 g of tetrachloroethane and
26.0 g of trichlorosilane is passed through a tubular furnace at 500°C over a period
of 95 minutes. The condensate is a dark mobile liquid weighing 35.5 g. Distillation
of the condensate from a Claisen flask gives 3.3 g of \( \alpha, \beta \)-dichlorovinyltrichloro-
silane, boiling point 157-167°C, \( n^0_{D} = 1.4928 \). The yield is 15% of theoretical.

Trichloroethylene, like dichloroacetylene, reacts with trichlorosilane to form
dichlorovinyltrichlorosilane. The reaction in this case probably proceeds in two
stages:
It is interesting to note that when dichlorovinyltrichlorosilane is titrated with alkali, the chlorine atom in the \( \beta \)-position does not undergo cleavage. Obviously the presence of the double bond reduces the mobility of the chlorine atom in the \( \beta \)-position.

Preparation of \( \alpha, \beta \)-Dichlorovinyltrichlorosilane by the Reaction Between Dichloroacetylene and Trichlorosilane. In a tube furnace for elementary analysis, a glass tube with an inside diameter of 9 mm, provided at one end with a dropping funnel for introducing the mixture, and at the other end with a condenser and a condensate collector, is placed. The collector, to improve the cooling, placed in a mixture of ice and salt. The tube is filled with an inert filler for better heat transfer. A mixture of 35 g of dichloroacetylene and 25 g of trichlorosilane, both of which must first be distilled, is passed over a period of 3 hours through the tube. The temperature during the reaction is held at the level of 90°C.

The 50.3 g of condensate collected had an amber color. Distillation of the condensate in a column showed it to contain 34 g of \( \alpha, \beta \)-dichlorovinyltrichlorosilane, boiling point 157-168°C, and 5.3 g of unreacted trichlorosilane.

The hydrogen chloride liberated during the process of synthesis and absorbed in a trap filled with alkali, is titrated and is found to amount to 7.0 g instead of the theoretical 6.5 g.

The \( \alpha, \beta \)-dichlorovinyltrichlorosilane is able to add still another molecule of trichlorosilane; in so doing, hexachloro-1,2-dichloroethylenedisilane is formed:

\[
\begin{align*}
\text{CHCl}=\text{CCl}_3 & \quad \rightarrow \quad \text{HCl} + \text{CCl}_3=\text{CCl}_3 \\
\text{CCl}_3=\text{CCl}_3 + \text{HSiCl}_3 & \quad \rightarrow \quad \text{CHCl}=\text{CCl}_3=\text{SiCl}_3
\end{align*}
\]

Preparation of Hexa-Chloro-1,2-Dichloroethylenedisilane. A mixture of 13 g of trichlorosilane, 6.3 g of dichlorovinyltrichlorosilane, and 0.2 g of benzoyl peroxide
is heated in a sealed tube at 70-80°C for 65 hours.

Fractionation of the mixture gives 3.9 g (40%) of hexachloro-1,2-dichloroethylenedisilane; boiling point 98-103°C (4 mm); refractive index nD20 = 1.5158.

This compound is interesting because it contains a chlorine atom in the β-position with respect to one silicon atom, and a chlorine atom in the α-position with respect to the other silicon atom. On titration with alkali it can be established that the cleavage of seven chlorine atoms takes place from this product. The reaction with alkali probably proceeds as follows:

\[
\text{Cl}_4\text{SiCHCICHCHCICl}_5 + 7\text{NaOH} \rightarrow \text{Si(OH)}_4 + \text{CHCl} = \text{CHSi(OH)}_2 + 7\text{NaCl}
\]

On reaction with methanol, only six chlorine atoms react:

\[
\text{Cl}_4\text{SiCHCICHCHCICl}_5 + 6\text{CH}_3\text{OH} \rightarrow (\text{CH}_3\text{O})_2\text{SiCHCICHCHCICl}_5(\text{CH}_3\text{O})_2 + 6\text{HCl}
\]

On hydrolysis of an ether solution of hexachloro-1,2-dichloroethylenedisilane, products completely soluble in water are formed.

The chlorination of dichlorovinyltrichlorosilane yields tetrachloroethyltrichlorosilane:

\[
\text{CHCl} = \text{CCl}_3\text{SiCl}_4 + \text{Cl}_2 \rightarrow \text{CHCl}_2\text{CCl}_3\text{SiCl}_3
\]

**Preparation of Tetrachloroethyltrichlorosilane.** A mixture of 8.5 g of dichlorovinyltrichlorosilane and 10.0 g of chloroform is placed in a pyrex test tube and submerged in ice. Dry chlorine is passed into the test tube until its gain in weight is 1.2 g. The liquid takes on a yellow tinge, and as soon as the test tube is taken out of the ice and placed in the sunlight, an energetic reaction at once begins.

The test tube is again cooled and chlorine is passed in until 1.4 g of chlorine has been absorbed. The reaction is again initiated by placing the test tube in sunlight. This operation is once more repeated, this time until the 6.5 g of chlorine has been absorbed and when the test tube is placed in the sunlight this time the reaction is
no longer as energetic, and the solution does not change its color. After standing
three days at room temperature, the product loses its color (probably owing to the
substitution of chlorine for hydrogen in the chloroform). The chloroform is distill-
ed off and the colorless residue is distilled in vacuo from a Claisen flask. The
principal fraction consists of tetrachloroethyltrichlorosilane; boiling point
104-106°C (17 mm), refractive index nD^21 = 1.5149.

The titration of α, β-tetrachloroethyltrichlorosilane with alkali leads to the
cleavage of four chlorine atoms in the form of sodium chloride, and of the organic
radical in the form of trichloroethylene:

\[
\text{CHCl}_2\text{CCl}_2\text{SiCl}_4 + 4\text{NaOH} \rightarrow \text{CHCl}=\text{CCl}_2 + \text{Si(OH)}_4 + 4\text{NaCl}
\]

Tetrabromomethyltrichlorosilane behaves similarly on hydrolysis in an alkaline medium.

By cautious hydrolysis of an ether solution of tetrachloroethyltrichlorosilane
by water, a viscous polymer of the composition \((\text{CHCl}_2\text{CCl}_2\text{SiCl}_1.5)_x\) may be separated; when heated to 110°C it gradually loses chlorine.

Under the action of alcohols on dichlorovinyltrichlorosilane, the corresponding
substituted esters are formed:

\[
\text{CHCl}=\text{CClSiCl}_4 - 3\text{CH}_2\text{OH} \rightarrow \text{CHCl}=\text{CClSi(OCCH)}_3 + 3\text{HCl}
\]

**Physical Properties**

The haloalkylhalosilanes are liquids that can be distilled without decomposition.
The haloarylhalosilanes are also mostly liquids; pentachlorophenyltrichlorosilane
and dibromophenyl dichlorosilane, which are separated in the crystalline form, are
exceptions.

Table 63 gives the physical properties of haloalkyl-(haloaryl)-halosilanes.
Table 63

Physical Properties of Haloalkyl-(Haloaryl)-Halosilanes

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c)</th>
<th>d)</th>
<th>e)</th>
<th>f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trichloromethyltrichlorosilane</td>
<td>CCl₂SiCl₄</td>
<td>155–156</td>
<td>87–92</td>
<td>(55 mm)</td>
<td>119,120,126</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>119,120,126</td>
<td></td>
</tr>
<tr>
<td>a,β-Dichlorovinyltrichlorosilane</td>
<td>CH₂=CHSiCl₂</td>
<td>163,5–164</td>
<td>1,56</td>
<td>1,4986</td>
<td>131</td>
</tr>
<tr>
<td>β,β-Dichlorovinyltrichlorosilane</td>
<td>CH₂=CHSiCl₂</td>
<td>162,5–163</td>
<td>1,4942</td>
<td>131</td>
<td></td>
</tr>
<tr>
<td>α-Chloroethyltrichlorosilane</td>
<td>CH₃CHClSiCl₂</td>
<td>138</td>
<td>—</td>
<td>—</td>
<td>122,129</td>
</tr>
<tr>
<td>β-Chloroethyltrichlorosilane</td>
<td>CH₃BrCH₂BrSiCl₂</td>
<td>152</td>
<td>—</td>
<td>—</td>
<td>122,129</td>
</tr>
<tr>
<td>β,β-Dichloro-α,β-dibromoethyltrichlorosilane</td>
<td>CH₂BrCH₂BrSiCl₂</td>
<td>104–106</td>
<td>1,5149</td>
<td>125,128,129</td>
<td></td>
</tr>
<tr>
<td>Tetrachloroethyltrichlorosilane</td>
<td>Cl₄C₂H₂SiCl₂</td>
<td>147–151</td>
<td>1,461</td>
<td>—</td>
<td>123</td>
</tr>
<tr>
<td>Chlorallyltrichlorosilane</td>
<td>CH₂CH₂CHClSiCl₂</td>
<td>157</td>
<td>—</td>
<td>—</td>
<td>123</td>
</tr>
<tr>
<td>α-Chloropropyltrichlorosilane</td>
<td>CH₂CH₂CH₂CH₃SiCl₂</td>
<td>178–178,5</td>
<td>—</td>
<td>—</td>
<td>123</td>
</tr>
<tr>
<td>β-Chloropropyltrichlorosilane</td>
<td>CH₂CH₂CH₂CH₂SiCl₂</td>
<td>165–166</td>
<td>—</td>
<td>—</td>
<td>123</td>
</tr>
<tr>
<td>γ-Chloropropyltrichlorosilane</td>
<td>CH₂CH₃SiCl₂</td>
<td>105</td>
<td>—</td>
<td>—</td>
<td>193</td>
</tr>
<tr>
<td>4-Chlorophenyltrichlorosilane</td>
<td>Cl₄C₂H₃SiCl₂</td>
<td>101–102</td>
<td>1,4543</td>
<td>193</td>
<td></td>
</tr>
<tr>
<td>2,3-Dichlorophenyltrichlorosilane</td>
<td>Br₃C₆H₄SiCl₂</td>
<td>120</td>
<td>—</td>
<td>—</td>
<td>223</td>
</tr>
<tr>
<td>4-Bromophenyltrichlorosilane</td>
<td>(Br₃C₆H₄OCH₂)₂SiCl₂</td>
<td>130–140</td>
<td>—</td>
<td>—</td>
<td>223</td>
</tr>
<tr>
<td>1-Bromo-5-methoxyphenyltrichlorosilane</td>
<td>C₆H₄CH₂CH₂CH₂Cl₂</td>
<td>243</td>
<td>—</td>
<td>—</td>
<td>128</td>
</tr>
<tr>
<td>α-Chlorobenzyltrichlorosilane</td>
<td>C₆H₄CH₃SiCl₂</td>
<td>112–114</td>
<td>1,5651</td>
<td>—</td>
<td>193</td>
</tr>
<tr>
<td>1,3,5-Trichlorophenyltrichlorosilane</td>
<td>C₆H₄Cl₃SiCl₂</td>
<td>125–126</td>
<td>1,653</td>
<td>—</td>
<td>193</td>
</tr>
<tr>
<td>Tetrachlorophenyltrichlorosilane</td>
<td>Cl₄C₆H₂SiCl₂</td>
<td>146–147</td>
<td>—</td>
<td>—</td>
<td>193</td>
</tr>
<tr>
<td>Pentachlorophenyltrichlorosilane</td>
<td>(Cl₄C₆H₂)₂SiCl₂</td>
<td>100,5</td>
<td>—</td>
<td>—</td>
<td>119,120,126</td>
</tr>
<tr>
<td>Di-(Chloromethyl)-dichlorosilane</td>
<td>CH₂Cl₃SiCl₂</td>
<td>109</td>
<td>—</td>
<td>—</td>
<td>127</td>
</tr>
<tr>
<td>Methyl-(trichloromethyl)-dichlorosilane</td>
<td>CH₃(CHCl)₂SiCl₂</td>
<td>121,3</td>
<td>—</td>
<td>—</td>
<td>127</td>
</tr>
<tr>
<td>Methylchloromethylidy-chlorosilane</td>
<td>CH₃CH₂Cl₂</td>
<td>107,2–107,8</td>
<td>—</td>
<td>—</td>
<td>127</td>
</tr>
<tr>
<td>Methylchloromethylidy-dichlorosilane</td>
<td>CH₃(CH₂Cl)₂SiCl₂</td>
<td>107,2–107,8</td>
<td>—</td>
<td>—</td>
<td>127</td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Boiling point; d) Specific gravity; e) Refractive index; f) Bibliography

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Chemical Properties

It was previously assumed that a halogen atom separated from the silicon atom even by a single oxygen atom behaves like an ordinary "aliphatic halogen atom". It is well known, for instance, that the halogen in \((\text{C}_2\text{H}_5)_2\text{Si}-\text{Cl}\) is capable of being saponified to form an alcohol, and under the action of potassium acetate may be replaced by an acetyl group, etc. Recent studies somewhat elaborate the question of the mutual influence between the atoms of halogens and silicon. It has been found, on more detailed study, that the influence of the silicon atom extends not only to a halogen atom in the \(\alpha\)-position with respect to silicon, but also to one in the \(\beta\)-position. This influence is manifested in the modification of the mobility of the halogen atom. The strength of the Si-C bond according to the position of the chlorine atom with respect to the silicon atom was investigated on the example of the \(\alpha\)-, \(\beta\)- and \(\gamma\)-chloropropyltrichlorosilanes. It was found that the mobility of the \(\alpha\)-halogen atom is approximately equal to its mobility in the alkyl chlorides. Thus, when \(\alpha\)-chloropropyltrichlorosilane is boiled for 2 hours with a normal solution of
alcoholic alkali (Bibl.80), almost complete cleavage of the chlorine atom in the 
$\alpha$-position takes place:

\[
\text{CH}_2\text{CH}_2\text{CHSiCl}_2\text{CHCISiCl}_2 + 4\text{NaOH} \rightarrow \text{CH}_2=\text{CHSi(OH)}_2 + 4\text{NaCl} + \text{H}_2\text{O}
\]

The $\alpha$-halogen atom does not react with an alcoholic solution of $\text{AgNO}_3$.

On treatment of $\alpha$-chloroethyldiethylchlorosilane with weak aqueous alkali, 
cleavage of the halogen does not occur, but $\alpha$-chloroethyldiethylhydroxysilane is 
formed instead:

\[
\text{CH}_2=\text{CH(CH}_2\text{CH}_2\text{SiCl}_2 + \text{NaOH} \rightarrow \text{CH}_2=\text{CH(CH}_2\text{CH}_2\text{SiOH} + \text{NaCl}
\]

Under the action of methylmagnesium bromide on $\alpha$-chloroethyldiethylchlorosilane 
$\alpha$-chloroethyldiethylmethylsilane is formed. A weak aqueous solution of alkali 
easily hydrolyzes $\beta$-chloroethyldichlorosilane, with cleavage of the $\beta$-chloroethyl 
group. $\gamma$-chloropropyldiethylchlorosilane occupied an intermediate position, with 
respect to resistance to hydrolysis, between the $\alpha$- and $\beta$-chloroethyldiethylchloro-
silane.

It has also been found that the addition of a halogen atom to an aliphatic radio-
dal attached to a silicon atom in turn exerts an influence on the behavior of the 
silicon atom and of the atoms attached to it. This is manifested particularly in the 
fact that the $\alpha$-haloalkyldialkylsilanols formed on the hydrolysis of $\alpha$-chloroalkyl-
dialkylchlorosilanes are more difficultly converted into siloxanes (Bibl.124). This 
influence of the halogen is more substantially expressed in the modification of the 
stability of the Si-C bond against the action of alkali. On adding to the radical, 
a halogen and certain other substituents, particularly electrophilic ones, make the 
Si-C bond unstable not only to the hydrolytic action of an alkali, but even to the 
anion of water. Such substituents include, besides halogen, the nitro and amino 
groups contained in phenyl radicals (Bibl.132).

The degree of the influence of a halogen in alkyl radical on the strength of
the Si–C bond depend on its position with respect to the silicon atom. The introduction of a halogen atom into an aliphatic radical in the $\beta$-position leads to a sharp decrease in the stability of the Si–C bond. A halogen atom in the $\gamma$-position weakens the Si–C bond to a smaller extent, and a halogen atom in the $\alpha$-position has still less of an effect in modifying the stability of the Si–C bond.

A halogen has an appreciable influence on the strength of the Si–C bond in $\alpha$-haloalkylhalosilanes only in the $\alpha$-halomethyl derivatives (Bibl.133).

Thus the chloromethyl derivative silanes, being stable against the action of acids, undergo quantitative cleavage of $\alpha$-chlorinated alkyl bonds under the action of such reagents as a strong solution of alkali, NaCN solution, and even water (in the case of trichloromethyltrichlorosilane), forming the corresponding hydrolysis products. Thus the presence of a chlorine atom in the methyl radical weakens the bond between the silicon and the organic radical. In this case, with increasing degree of chlorination of the radical, and accordingly also with increasing electropositivity of the carbon atom, the tendency of compounds to such hydrolysis appreciably increases. Thus, $\text{Cl}_2\text{C}_2\text{SiCl}_3$, on hydrolysis by water, is completely broken down with formation of chloroform and silicic acid. The monochlorinated methyl groups are more firmly attached to the silicon atom, but they likewise undergo cleavage, with formation of methyl chloride (when the compounds are boiled with an alcoholic solution of alkali).

The influence of a halogen atom in the alkyl group in the $\beta$-position with respect to the silicon atom on the stability of the Si–C bond will be seen from the following examples.

Titration of $\beta$-chlorothyltrichlorosilane (Bibl.50) with an 0.5 N solution of NaOH in 40% aqueous ethanol leads to the quantitative cleavage of the alkyl radical:

$$\text{CICH}_2\text{CH}_2\text{SiCl}_3 + 4\text{NaOH} \rightarrow \text{CH}_2=\text{CH}_2 + \text{Si(OH)}_4 + 4\text{NaCl}$$

Under the action of an ether solution of methy magnesium bromide on $\beta$-chlo-
ethyltrichlorosilane (Bibl.78), on heating 3 hours over a water bath, ethylene and tetramethylsilane in 54% yield is formed:

\[
\text{CICH}_2\text{CH}_3\text{SiCl}_4 + 4\text{CH}_2\text{MgBr} \rightarrow \text{CH}_2=\text{CH}_2 + \text{Si(CH}_3)_4 + 4\text{MgClBr}
\]

When \(\beta\)-chloroethyltriethylsilane reacts with 7.6 mols of ethylmagnesium bromide tetraethylsilane in 50% yield is formed.

A.D.Petrov has shown that \(\beta\)-chloroethylalkylsilanes enter into reaction with alkylmagnesium halides without appreciable cleavage of the halogen (Bibl.221).

Cautious hydrolysis of \(\beta\)-chloroethyltrichlorosilane by pouring an ether solution of it, prepared from 100 g of the product and 300 ml of ether, onto a mixture of 200 g of ice and 500 g of water, with stirring, over the period of 1 hour, followed by distilling the ether from the hydrolysis product, makes it possible to preserve the \(\beta\)-chloroalkyl group at the silicon atom. The brittle polymer so obtained is easily decomposed in the cold under the action of aqueous alkali:

\[
(\text{CICH}_2\text{H}_{13}\text{SiO})_x + x\text{NaOH} = x\text{C}_9\text{H}_6 + x\text{NaCl} + x\text{H}_2\text{O} + (\text{HOSiO})_y
\]

When \(\beta\)-chloro-propyltrichlorosilane reacts with 40% aqueous-alcoholic alkali, cleavage of propylene takes place (Bibl.22):

\[
\text{CH}_3\text{CHCICH}_3\text{SiCl}_4 + 4\text{NaOH} \rightarrow \text{Cl}_3\text{CH}=\text{CH}_2 + \text{Si(OH)}_4 + 4\text{NaCl}
\]

Under the same conditions, \(\beta\)-chloroethyl-diethylchlorosilane and \(\beta\)-chloroethyl-fluorosilane (Bibl.130) split off ethylene:

\[
\text{CICH}_2\text{CH}_2\text{Si(C}_9\text{H}_6)_3\text{X} + 2\text{NaOH} \rightarrow \cdot \text{CH}_2=\text{CH}_2 + \text{NaCl} + \text{NaX} + (\text{C}_9\text{H}_{13})\text{Si(OH)}_2
\]

The reaction proceeds to 98% of completion.

A similar reaction with 1.25 N aqueous alkali proceeds to 87% of completion.

\(\beta\)-chloroethyl-diethylchlorosilane and \(\beta\)-chloroethyl-diethylfluorosilane react with methylmagnesium bromide as follows (Bibl.82):
The yield of diethyldimethylsilane is respectively 57.5% and 59%.

When 33 g of $\beta$-chloroethyldiethylchlorosilane is added to a mixture of 150 g of pentane and 5 g of aluminum chloride, over a period of 1 hour, the following reaction takes place:

$$
\text{CICH_2CH}_2\text{Si(C_2H_5)_2 + 2CH_3MgBr} \rightarrow \text{CH}_2=\text{CH}_2 + (\text{C}_2\text{H}_5)\text{Si(C}_2\text{H}_5)_2 + \text{MgClBr} + \text{MgBr}_2
$$

Rectification of this mixture yields 21 g of diethyldichlorosilane. In the corresponding reaction, $\beta$-chloroethyldiethylfluorosilane forms not diethylfluorochlorosilane, but diethyldichlorosilane in 71% yield.

$$
\text{CICH}_2\text{CH}_2\text{Si(C}_2\text{H}_5)_2 \rightarrow \text{AlCl}_3
\text{(C}_2\text{H}_5)\text{SiCl}_2 + \text{CH}_2=\text{CH}_2 + \text{AlCl}_2\text{F}_2
$$

Tert-chlorobutyltrichlorosilane (Bibl.19) reacts with a 33% aqueous solution of KOH to form isobutylene in 94% of theoretical yield:

$$
\text{CH}_2\text{Cl(C}_2\text{H}_5)\text{C}=\text{SiCl}_4 + 4\text{KOH} = \text{CH}_2=\text{C}(\text{CH}_3)_2 + \text{Si(OH)}_4 + 4\text{KCl}
$$

When tert-chlorobutyltrichlorosilane reacts with water, isobutylene is also formed in 26% of theoretical yield:

The $\alpha$, $\beta$-polychlorosilanes react similarly with alkali:

$$
\text{Cl}_2\text{CHCClSiCl}_3 + 4\text{NaOH} = \text{Si(OH)}_4 + \text{CHCl} = \text{CCl}_2 + 4\text{NaCl}
\text{Cl}_2\text{Si(CHCl)}_2\text{CISiCl}_3 + 7\text{NaOH} = \text{Si(OH)}_4 + \text{CHCl} = \text{CHSi(OH)}_2 + 7\text{NaCl}
$$

It will be clear from this example how unstable is the bond between the silicon atom and the aliphatic radical with a chlorine atom in the $\beta$-position with respect to the silicon. The ease of cleavage of the radical is undoubtedly due to the fact that the silicon atom is more electropositive than the carbon atom. The process of cleavage of the radicals is related to the passage of electrons from the silicon atom,
and, for example, for the case of aluminum chloride, this process probably takes place according to the following mechanism:

\[
\begin{align*}
-\text{Si}-\text{CH}_2\text{CH}_2\text{Cl} & + \text{AlCl}_3 \rightarrow -\text{SiCH}_2\text{CH}_2^+ + \text{AlCl}_4^- \\
-\text{Si}-\text{CH}_2\text{H}_2^+ & \rightarrow \text{H}_2 = \text{CH}_2 + -\text{Si}^+ \\
-\text{Si}^+ \cdot \text{AlCl}_4^- & \rightarrow -\text{Si} \cdot \text{AlCl}_4
\end{align*}
\]

The transition of electrons is facilitated owing to the presence of such nucleophilic groups as the hydroxy or amino groups. It is with this that the ease of cleavage of the radical in the hydrolysis of the chloroalkylchlorosilane is connected, as well as the ease of cleavage of the chloroalkylaminosilanes:

\[
\begin{align*}
\text{R-Si-CH}_2\text{CH}_2\text{Cl}+X^- & \rightarrow \text{RSi-R} + (\text{CH}_2\text{CH}_2\text{Cl})^- \\
\text{(CH}_2\text{CH}_2\text{Cl})^- & \rightarrow \text{CH}_2=\text{CH}_2 + \text{Cl}^- \\
\text{RSi-R}+\text{Cl}^- & \rightarrow \text{RSi-Cl} + (X)^-
\end{align*}
\]

where X is a hydroxy or amino group. If there are no nucleophilic groups in the reaction medium (for instance on the decomposition of tetra-substituted silanes with a chlorine atom in the β-position), the process proceeds incomparably more slowly, and the -Si-C bond proves to be more stable.

Another interesting example is the reaction between β-chloroethyltrichlorosilane and quinoline. Owing to the inability of a tertiary base to form a negative ion, the -Si-C bond is preserved, and as a result of the reaction, even at an elevated temperature, an alkylhalosilane with an unsaturated radical is formed:
Interesting observations were made in a comparison of the resistance of \( \alpha \) and \( \beta \)-chloroethyltrichlorosilane to pyrolysis and to the action of quinoline (Bibl.134). The portions of the chloroethyltrichlorosilane taken for the reaction was 110 g in each case. The results of the study were as follows:

<table>
<thead>
<tr>
<th>Reaction with Quinoline</th>
<th>( \text{CH}_2\text{CHClSiCl}_3 )</th>
<th>( \text{CH}_2\text{ClCH}_2\text{SiCl}_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Starting product, g</strong></td>
<td>110</td>
<td>110</td>
</tr>
<tr>
<td><strong>Yield of ( \text{SiCl}_4 ), g</strong></td>
<td>7.3</td>
<td>1.7</td>
</tr>
<tr>
<td><strong>Yield of ( \text{CH}_2 = \text{CHSiCl}_3 ), g</strong></td>
<td>10.8</td>
<td>38</td>
</tr>
<tr>
<td><strong>Residue of starting product, g</strong></td>
<td>46</td>
<td>9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pyrolysis at 610°C</th>
<th>( \text{CH}_2\text{CHClSiCl}_3 )</th>
<th>( \text{CH}_2\text{ClCH}_2\text{SiCl}_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Starting product, g</strong></td>
<td>110</td>
<td>110</td>
</tr>
<tr>
<td><strong>Yield of ( \text{SiCl}_4 ), g</strong></td>
<td>6.5</td>
<td>37</td>
</tr>
<tr>
<td><strong>Yield of ( \text{CH}_2 = \text{CHSiCl}_3 ), g</strong></td>
<td>17.5</td>
<td>16</td>
</tr>
<tr>
<td><strong>Residue of starting product, g</strong></td>
<td>44.5</td>
<td>11</td>
</tr>
</tbody>
</table>

It is clear from these data that \( \beta \)-chloroethyltrichlorosilane is a more reactive compound than \( \alpha \)-chloroethyltrichlorosilane.

Ethyltrichlorosilane and vinyltrichlorosilane under similar conditions are stable; \( \beta \), \( \gamma \)-dichloropropyltrimethylsilane forms trimethylchlorosilane and allyl chloride, while \( \beta \)-bromopropyltrimethylsilane, at temperatures over 40°C, forms propylene and trimethylbromosilane.

The behavior of \( \alpha \), \( \beta \)-dichloroethylene under the action of a high temperature and of quinoline have also been studied in detail.

The results of this work are shown in the following diagram:
Diagram of the Transformations of α, β-Dichloroethyltrichlorosilane

\[
\text{CH}_2\text{CH}_2\text{SiCl}_3 \xrightarrow{610 ^\circ \text{C}} \text{SiCl}_4 + \text{CHCl} = \text{CHSiCl}_3 + \text{CH}_2\text{CCl}_3 \cdot \text{HCl}
\]

\[
\text{CH}_2\text{BrCClBrSiCl}_3 \xrightarrow{610 ^\circ \text{C}} \text{SiCl}_4 + \text{CHCl} = \text{CHSiCl}_3 + \text{CH}_2\text{CCl}_3 \cdot \text{HCl}
\]

\[
\text{BrCHClCHBrSiCl}_3 + \text{CH}_2\text{BrCClBrSiCl}_3
\]

\[
\text{OH}^- \xrightarrow{610 ^\circ \text{C}} \text{CH}_2 = \text{CHCl} \quad \text{CH}_2\text{=CHCl} \quad \text{SiCl}_4
\]

\[
\text{OH}^- \xrightarrow{610 ^\circ \text{C}} \text{CH}_2 = \text{CHCl} \quad \text{SiCl}_4
\]

\[
\text{OH}^- \xrightarrow{610 ^\circ \text{C}} \text{CH}_2 = \text{CHCl} \quad \text{SiCl}_4
\]

\[
\text{BrCHClCHBrSiCl}_3 + \text{CH}_2\text{BrCClBrSiCl}_3
\]

\[
\text{BrCHClCHBrSiCl}_3 + \text{CH}_2\text{BrCClBrSiCl}_3
\]

\[
\text{BrCHClCHBrSiCl}_3 + \text{CH}_2\text{BrCClBrSiCl}_3
\]
The pyrolysis of $\alpha, \beta$-dichloroethyltrichlorosilane leads to the formation of hydrogen chloride, $\text{SiCl}_4$, and a mixture of $\alpha$- and $\beta$-chlorovinyltrichlorosilanes. Vinylchloride is not formed on this reaction. The addition of bromine to a mixture of chlorovinyltrichlorosilanes leads correspondingly to a mixture of dibromochloroethyltrichlorosilanes.

It was shown earlier that if two atoms of a halogen (chlorine and bromine) are in position 2 with respect to the silicon atom, then in the process of the halogenation, the cleavage of the bromine takes place more readily than that of the chlorine. When the mixture of dibromochloroethyltrichlorosilanes so obtained was treated with bases, 1,1-chlorobromoethylene was formed (and rapidly polymerized under the reaction conditions), together with 1-chloro-2-bromoethylene, which did not polymerize. Although the above mentioned bromochloroethylenes were not liberated as individual compounds, but was obtained in mixtures of other products, these data point precisely to such a mechanism of the process.

In contrast to pyrolytic cleavage, the treatment of dichloroethyltrichlorosilane with quinoline leads to the formation of $\text{SiCl}_4$ and 1-chlorovinyltrichlorosilane. The isomeric product, that is, 2-chlorovinyltrichlorosilane, was not detected, although its formation was to be expected as well. The pyrolysis of 1-chlorovinyltrichlorosilane led to the formation of $\text{SiCl}_4$, acetylene, and, to a certain extent, the starting material remained unchanged. On the cleavage of the organic radical by the action of aqueous alkali, vinyl chloride was formed, which was identified in the form of 1,1-chlorobromo-2-bromoethane. The position of the chlorine in 1-chlorovinyltrichlorosilane was determined by addition of bromine and treatment with alkali, as a result of which a certain amount of 1-bromo-1-chloroethylene was obtained.

Pyrolysis of 1,1-chlorobromo-2-bromoethyltrichlorosilane gave a small amount of $\text{SiCl}_4$, of the original compound, and of a halovinyltrichlorosilane of unknown structure.

Addition of chlorine to 1-chlorovinyltrichlorosilane gave 1,1,2-trichloroethyl-
Trichlorosilane. Its structure was demonstrated by cleavage of vinylidene chloride under the action of alkali. Pyrolysis of 1,1,2-trichloroethyltrichlorosilane at 610°C led to the formation of SiCl₄ and of symmetrical dichloroethylene.

Pyrolysis of 1,1,2-trichloroethylchlorosilane, in a medium of trichloroethylene as diluent, led to the same results. Cleavage of HCl by the aid of quinoline also led to the formation of SiCl₄ and 1,1-vinlyidine chloride, identified in the form of 1,1-dichloro-1,2-dibromoethylene.

1,2-dichloroethyltrichlorosilane may possibly also be an intermediate product in the reaction between trichlorosilane and sym-dichloroethylene:

\[ \text{CICH} = \text{CHCl} + \text{HSiCl}_3 \rightarrow \text{CICH}_2\text{CHSiCl}_3 \]

The heating of a mixture of cis- and trans-1,2-dichloroethylenes with trichlorosilane led to the formation mainly of 2-chlorovinyltrichlorosilane, possibly with an admixture of a small amount of 1-chlorovinyltrichlorosilane. As a result of the addition of bromine to the pyrolysis product of the compound so obtained, 1-bromo-2,2-chlorobromoethyltrichlorosilane was formed, and broke down under the action of alkali with the formation of 1-chloro-2-bromoethylene. When a mixture of vinylidene chloride was reacted with trichlorosilane at a high temperature, 1- or 2-chlorovinyltrichlorosilane in very low yield was obtained. Compounds containing unsaturated and saturated radicals attached to the silicon atom were obtained by the action of the corresponding organomagnesium compounds on allyl- or vinyltrichlorosilane. Thus, phenylvinyl dichlorosilane, benzylvinyl dichlorosilane, allylphenyldichlorosilane, etc, were prepared (Bibl.60).

As already stated, the chlorine atom in the γ-position also weakens the bond between the alkyl radical and the silicon atom, but this influence is considerably less pronounced than it is in the β-chloroalkylchlorosilanes. Thus, for instance, the titration of γ-chloropropyltrichlorosilane with 0.5 N alcoholic alkali leads to the formation of a hydrolysis product that completely preserves the chloropropyl...
group, but heating with alkali leads to the cleavage of cyclopropane:

\[
\text{ClC} = \text{CHCH}_2\text{SiCl}_3 + 4\text{KOH} \rightarrow \text{CH}_3 \quad \text{Si(OH)}_4 + 4\text{KCl}
\]

Hydrolysis of \(\gamma\)-Chloropropyltrichlorosilane. To a solution of 38 g of KOH in 100 ml of absolute ether, 24.6 g of \(\gamma\)-chloropropyltrichlorosilane is gradually added. After the addition has been completed, the mixture is heated under a reflux condenser, a solution of 28 g of dry KOH in 150 ml of water is added to it, and the mixture is again boiled. During the process of reaction, 910 ml (91\%) of gaseous cyclopropane is collected.

The unsaturated alkylchlorosilanes containing a chlorine atom in the \(\beta\)-position are more stable compounds than the corresponding saturated compounds (Bibl.138); thus \(\beta, \beta\)-dichlorovinyltrichlorosilane, on reacting with aqueous alkali in the cold, does not split off the organic radical:

\[
\text{Cl}_2\text{C} = \text{CHSiCl}_3 + 3\text{NaOH} \rightarrow \text{Cl}_2\text{C} = \text{CHSi(OH)}_3 + 3\text{NaCl}
\]

On reactions with organomagnesium compounds, the Si-C bond likewise remains intact:

\[
\text{Cl}_2\text{C} = \text{CHSiCl}_3 + 3\text{CH}_2\text{MgBr} \rightarrow \text{CCl}_3 = \text{CHSi(Cl)}_3 + 3\text{MgClBr}
\]

Heating with alkali does cause cleavage of the Si-C bond:

\[
\text{Cl}_2\text{C} = \text{CHSiCl}_3 + 3\text{KOH} + \text{H}_2\text{O} \rightarrow \text{Cl}_2\text{C} = \text{CH}_2 + \text{Si(OH)}_3 + 3\text{KCl}
\]

Hydrolysis of Dichlorovinyltrichlorosilane. To a solution of 300 g of caustic potash in 700 ml of water, 114 g of dichlorovinyltrichlorosilane is added, the mixture is heated a few minutes, and the dichloroethylene is then distilled off with steam. \(\alpha, \beta\)-dichlorovinyltrichlorosilane reacts similarly.

The process of cleavage proceeds by a mechanism similar to that described above.
for the saturated chloroalkylchlorosilanes; and the attachment of a nucleophilic hydroxyl ion plays a substantial role here as well.

Dichlorovinyltrichlorosilane reacts with ethylmagnesium bromide to form di-
dichlorovinyltriethylsilane:

\[
\text{CICH} = \text{CClSiCl}_2 + 3\text{C}_2\text{H}_4\text{MgBr} \rightarrow \text{CHC} = \text{CClSi(C}_2\text{H}_8) + 3\text{MgClBr}
\]

In this case as well, the inertness of the chlorine atom at the double bond manifests itself. It should be remembered that under the action of ethylmagnesium bromide and \( \beta \)-chloroethyl dichlorosilane, cleavage of the molecule takes place, liberating ethyl-

cenes:

\[
\text{CICH}_2 - \text{CH}_2\text{SiCl}_3 + 4\text{C}_2\text{H}_4\text{MgBr} \rightarrow \cdot \text{Si(C}_2\text{H}_4)_4 + \text{CH}_2 = \text{CH}_2 + 4\text{MgClBr}
\]

Chemical properties of the polychloromethylsiloxanes. To study the behavior of the chlorinated polymethylsiloxanes, heptamethylchloromethylcyclotetrasiloxane, pentamethylchloromethyl disiloxane, and tetramethyl-1, 2-, bis-dichloromethyl disiloxane were prepared.

Preparation of Chlorinated Polymethylsiloxanes. Heptamethylchloromethylcyclotetrasiloxane was prepared by direct chlorination of octamethylcyclotetrasiloxane by chlorine under ultraviolet irradiation. Direct chlorination of hexamethyl disiloxane did not lead to a positive result. Instead of the expected product, pentamethyl-
chloromethyl disiloxane, an equilibrium system was formed by the reaction:

\[
(\text{CH}_3)_5\text{SiOSi(CH}_3)_2 + 2\text{HCl} \rightleftharpoons \text{H}_2\text{O} + 2(\text{CH}_3)_3\text{SiCl}
\]

Pentamethylchloromethyl disiloxane was then prepared by cohydrolysis of dimethyl-
chloromethylchlorosilane with trimethylchlorosilane.

Tetramethyl-1, 2-, bis-(dichloromethyl)-disiloxane was obtained as a result of the hydrolysis of dimethyldichloromethylchlorosilane. When these products were boiled with water or with aqueous dioxane, they remained unchanged. If these products are
boiled instead with a solution of caustic potash in butanol, hydrolysis does take place, with cleavage of methyl chloride. A hydroxyl group takes the place of the chloromethyl group, and this hydroxyl group under the reaction conditions, forms a siloxane bond. When the cleavage reaction is conducted with certain precautions, it is possible to liberate from heptamethylchloromethyldicyclosil).oxy a substance with a structure of two rings with four silicon atoms in each, connected by a siloxane bridge.

The second product formed under the action of aqueous alkali on heating, likewise splits off methyl chloride. The third product splits off methylene chloride only when heated with an alcoholic solution of alkali. Experiments to determine the relative rates of hydrolysis of the first and third products under the action of a 10% solution of caustic potash in a medium of butanol showed that the first product is 88% hydrolyzed after 15 minutes, while the third product is 80% hydrolyzed. Even such weak bases as an alcoholic solution of ammonia split off the chloromethyl groups. For instance, pentamethylchloromethyldisiloxane, on standing with a weak solution of ammonia, forms pentamethyldihydroxydisiloxane. Methylchloride is liberated at the same time. Or boiling pentamethylchloromethyldisiloxane with an alcoholic solution of sodium cyanide, an insoluble gel is formed.

The chlorine atoms in the organic radicals of the hexaalkyldisiloxanes may be replaced by various functional groups. When metallic magnesium reacts with pentamethylchloromethyldisiloxane in an ether solution, organomagnesium compounds are formed, which decompose on treatment with solid carbon dioxide to form the magnesium salt of acetoxyethylpentamethyldisiloxane, from which the free acid may be liberated by acidifying the reaction mixture. The product is recrystallized from pentane to purify it. The yield is 85% of theoretical (Bibl.134):

\[
\begin{align*}
(CH_3)_3SiOSi(CH_3)CH_2Cl + Mg &\rightarrow (CH_3)_3SiOSi(CH_3)CH_2MgCl + CO_2 \\
(CH_3)_3SiOSi(CH_3)CH_2COOMgCl &\rightarrow (CH_3)_3SiOSi(CH_3)CH_2COOH + MgCl_2
\end{align*}
\]
When pentamethylchloromethyl disiloxane is boiled with a small excess of potassium acetate in an equal volume of glacial acetic acid, acetoxy methylpentamethyldisiloxane is formed (Bibl.135).

\[
(\text{CH}_3)_5\text{SiOSi(\text{CH}_3)_3\text{CH}_3} + \text{CH}_3\text{COOK} \rightarrow \text{KCl} + (\text{CH}_3)_3\text{SiOSi(\text{CH}_3)_3\text{CH}_3}\text{COCH}_3
\]

At the same time, as a result of rearrangement, hexamethyldisiloxane and sym-1,2-acetoxymethyltetramethyldisiloxane are formed. The yield of the main reaction product is 50%. When potassium acetate and 1,2-chloromethyltetramethyldisiloxane react under similar conditions, 1,2-acetoxymethyltetramethyldisiloxane is formed in almost quantitative yield.

**Hydrolysis of Alkyl-(Aryl)-Chlorosilanes and Haloalkyl-(Haloaryl)-Chlorosilanes**

Under the action of water on alkyl- or arylchlorosilanes, hydrolytic cleavage of the chlorine atoms takes place, with formation of unstable intermediate products of hydrolysis: trialkyl-(aryl)-silanols, dialkyl-(aryl)-silanediols, and alkyl-(aryl)silanetriols; in the monomeric form, trialkylsilanols, dialkyl- and diarylsilanediols, phenylsilanetriols, and dichlorophenylsilanetriol are known.

\[
\text{R}_3\text{SiCl} + \text{H}_2\text{O} \rightarrow \text{R}_3\text{SiOH} + \text{HCl}
\]
\[
\text{R}_4\text{SiCl}_2 + 2\text{H}_2\text{O} \rightarrow \text{R}_4\text{Si(OH)}_2 + 2\text{HCl}
\]
\[
\text{R}_5\text{SiCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{R}_5\text{Si(OH)}_3 + 3\text{HCl}
\]

In the presence of HCl, hydrolysis always leads to the formation of condensation products: in the first case, of disiloxane, in the second case, of linear or cyclic polysiloxanes, and in the third case, of branched polysiloxanes (Bibl.133).

The velocity of hydrolysis of the alkylchlorosilanes is so high that the products of partial hydrolysis and condensation
can be prepared only when special methods are used. The composition and properties of the polymeric products formed as a result of hydrolysis depend to a considerable degree on the reaction conditions, the acidity of the medium, the presence of a solvent, its polarity, etc. Thus, for instance, on the hydrolysis of methyltrichlorosilane by ice water or steam in the presence of a solvent, an infusible amorphous substance of the empirical composition \((RSiO_{1.5})_n\) is formed. If the hydrolysis of methyltrichlorosilane is conducted by gradually pouring it into an emulsion of water and butanol, with good stirring, a viscous resinous substance soluble in organic solvent is formed, and when heated for a short time at 150°C this substance loses its fusibility and solubility in inorganic solvents. Such a difference in the properties of the products formed as a result of almost the same chemical processes may be explained by the view that, on the introduction of the methylchlorosilane into the water-alcohol emulsion, three processes, competing among themselves, take place simultaneously in the system water-methyltrichlorosilane-butanol, and that the velocities of these reactions differ substantially from each other (Bibl.139):

\[
\begin{align*}
(\text{CH}_3\text{SiCl}_3 + 3\text{H}_2\text{O}) & \rightarrow \text{CH}_3\text{Si}((\text{OH})_3 + 3\text{HCl} \quad \text{(1)} \\
\text{CH}_3\text{SiCl}_3 + 3\text{C}_4\text{H}_9\text{OH} & \rightarrow \text{CH}_3\text{Si}((\text{OC}_4\text{H}_9)_3 + 3\text{HCl} \quad \text{(2)} \\
\text{CH}_3\text{Si}((\text{OC}_4\text{H}_9)_3 + 3\text{H}_2\text{O} & \rightarrow \text{CH}_3\text{Si}((\text{OH})_2 + 3\text{C}_4\text{H}_9\text{OH} \quad \text{(3)}
\end{align*}
\]

While the velocities of the first two reactions are close together, the third reaction proceeds considerably more slowly. As a result, this process proceeds according to the following mechanism:

\[
\begin{align*}
\text{CH}_3\text{SiCl}_3 + 2\text{H}_2\text{O} + \text{C}_4\text{H}_9\text{OH} & \rightarrow \text{CH}_3\text{Si}((\text{OH})_n + 3\text{HCl} \quad \text{(4)} \\
\text{CH}_3\text{Si}((\text{OH})_n & \rightarrow \text{CH}_3\text{Si}((\text{OH})_2 + 3\text{C}_4\text{H}_9\text{OH} \quad \text{(5)}
\end{align*}
\]

The number of butoxy groups in the polymer is determined by the ratio between
the amounts of methyltrichlorosilane, water and butanol taken into the reaction. In practice, their content in the polymer ranges from 0.1 to 0.3 to each silicon atom. Their fundamental significance, however, consists in the fact that, by blocking some of the points where hydroxyl groups can be formed, the butoxy groups hinder the possible growth of the molecule in the transverse direction.

Similar phenomena take place in the hydrolysis of methyltrichlorosilane by an aqueous solution of alkali taken in excess (for instance, 4 mols per mol of ethyltrichlorosilane). In this reaction, the sodium atoms act as the blocking factors, forming silanolate groups in the polymer, which prevent the growth of the molecules in the transverse direction.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_2 \quad \text{CH}_3 \\
\text{HO-Si} & \quad \text{O-Si} \quad \text{O-Si-OH} \\
\text{ONa} & \quad \text{ONa} \quad \text{ONa} \\
\end{align*}
\]

The influence of the polarity of the solvent on the process of hydrolysis of alkylhalosilanes has been investigated only in the general form. On the hydrolysis of alkyltrihalosilanes by water in the absence of active solvents, ether, dioxane, or alcohols, infusible and insoluble polymeric products are formed in the shape of amorphous precipitates. The presence of inert solvents, benzene, toluene, etc, has no effect on the properties of the product obtained. Since the primary product of hydrolysis, the alkylsilanetriols, are substances readily soluble in water, alcohols, and ethers, the process of condensation of the monomeric molecules, in the absence of active solvents, proceeds at high velocity in the aqueous phase, and the polymer so formed is thrown down as a precipitate.

In the presence of active organic solvents, which dissolve both monomeric and polymeric products, the condensation takes place in the organic layer, in a homogeneous medium, which excludes the possibility of precipitation. For practical purposes, mixtures of active solvents, alcohols or ether, with inactive aromatic hydrocarbons, are used in the hydrolysis of alkyltrihalosilanes. The properties of the polymers also depends on the functionality of the system causing the condensation.
The resins formed on the hydrolysis and condensation of alkyl- or aryltrichlorosilanes are of the structure (171,140,141):

\[
\begin{array}{c}
\text{R} \quad \text{R} \\
\text{O-Si-O-Si-O-} \\
\text{O} \quad \text{O}
\end{array}
\]

The presence of oxygen bridges between the chains is responsible for the formation of infusible, insoluble polymers by even a brief thermal treatment.

With increasing number of organic radicals per silicon atom, the capability of the polymers to pass into the infusible and insoluble state is lessened: on condensation of bifunctional molecules, only linear or cyclic polymers are formed. On the hydrolysis and condensation of monofunctional molecules of the type \( \text{R}_3\text{SiCl} \), dimers are formed, low-molecular compounds of the type \( \text{R}_3\text{SiCsir}_3 \). In themselves, these products are not of great interest, but the reaction of cohydrolysis and cocondensation of bifunctional or trifunctional molecules with monofunctional ones make it possible to obtain polymers with a different and predetermined chain length, depending on the molecular ratios of the component taken into the reaction. On cohydrolysis and cocondensation between phenyltrichlorosilane and a dialkyldichlorosilane, resins are formed which have a higher elasticity than the resin formed on the hydrolysis and condensation of phenyltrichlorosilane alone. An investigation of the structure of these resins shows that the number of cross-linking bonds between the polymer chains in the former case is smaller than in the latter case. It is this circumstance that leads to the increased elasticity of the resins. The structure of the resins obtained by cohydrolysis and cocondensation may be schematically expressed as follows:

\[
\begin{array}{c}
\text{R} \quad \text{R'} \\
\text{O-Si-O-Si-O-} \\
\text{O} \quad \text{O'}
\end{array}
\]

A special classification must be reserved for the resins whose molecular chains
are built up of alternating siloxane and hydrocarbon units, as, for instance.

\[
\begin{array}{c}
R \quad R \quad R \\
\big(-\big)\quad \text{Si-} (\text{CH}_2)\text{Si-O-} \quad \text{Si-CH}_2 \\
R \quad R \quad R
\end{array}
\]

Such polymers have not yet been well studied, but their structure allows us to expect them to combine the properties of organic and organopolysiloxane resins.

The velocity of the condensation reaction depends on the concentration of the hydroxyl groups in the condensing system, on the temperature, and on the character and number of the organic radicals attached to the silicon atom. Thus, for instance, monomeric orthosilicic acid is known only at temperatures below -20°C, while for the complete conversion of orthosilicic acid to the condensed state, (SiO\textsubscript{2})\textsubscript{n}, prolonged heating at 1000°C is necessary. Similarly, the initial stage of condensation of organosilicon monomers proceeds so rapidly that only C\textsubscript{6}H\textsubscript{5}Si(OH)\textsubscript{3} and Cl\textsubscript{2}C\textsubscript{6}H\textsubscript{3}Si(HO)\textsubscript{3} are liberated from compounds of the type RSi(OH)\textsubscript{3} (Bibl.19). As in the case of orthosilicic acid, it is very difficult to remove the last hydroxyl groups from polymers with a rather long chain, and the use of energetic dehydrating agents, such as sulfuric acid, esters of boric acid, etc., is required for this purpose. Compounds of the type R\textsubscript{3}SiOH are considerably more stable and may be distilled under atmospheric pressure without any signs of condensation.

The size of the organic radical attached to the silicon atom also exerts a substantial influence on the velocity of the process of hydrolysis and condensation. As a rule, the velocity of the condensation reaction decreases with increasing molecular weight of the organic radical. At the same time, owing to the enlargement of the organic part, the heat resistance of the polymer is somewhat lowered. The polyphenylsiloxane resins are an exception to this rule, being distinguished by high thermal stability and resistance to oxidation by the oxygen of the air at elevated temperatures.
Hydrolysis of Monofunctional Compounds

Monofunctional compounds of the type $R_3SiX$, as stated above, have no independent practical importance for the preparation of organosilicon polymers, but are used to form polymers of a definite structure and composition by their cocondensation with di-, tri-, and tetra-functional compounds.

The trialkylhalosilanes are readily hydrolyzed by water, forming hexaalkylsiloxanes. The trialkylfluorosilanes are considerably more stable, and are hydrolyzed more slowly than other halo-derivatives (Bibl.142, 143). The first representative of the class of hexaalkylsiloxanes, hexamethyldisiloxane, is formed on hydrolysis of trimethylchlorosilane in an acid medium (Bibl.144, 145, 146):

$$2(CH_3)SiCl + H_2O \rightarrow (CH_3)_2SiOSi(CH_3)_2 + 2HCl$$

Hexamethyldisiloxane is a liquid of boiling point 100°C, partially soluble in water. The siloxane bond in the hexaalkylsiloxanes is weakened in some degree by the presence of three organic radicals attached to the silicon atom. The reverse transition from hexamethyldisiloxane to such trimethylhalosilanes as $(CH_3)_3SiF$ and $(CH_3)_3SiCl$ may be accomplished by the action of anhydrous hydrogen halides in the presence of concentrated sulfuric acid. Ammonium fluoride or chloride or the corresponding sodium salts, which liberate the hydrogen halide on reaction with sulfuric acid, are usually used in practice for this purpose (Bibl.36, 137, 139).

**Preparation of Trimethylfluorosilane from Hexamethyldisiloxane.** To 196 g of strong sulfuric acid 81 g of hexamethyldisiloxane is added with stirring and ice cooling. Then the reaction mixture is slightly warmed on the water bath and 48.1 g of ammonium chloride is gradually added. The trimethylfluorosilane liberated is caught by ether (Bibl.146).

**Preparation of Trimethylchlorosilane from Hexamethyldisiloxane.** To a mixture of 324 g of hexamethyldisiloxane and 1000 g of concentrated sulfuric acid, 321 g of dry finely ground ammonium chloride is gradually added over a period of 3 hours,
at 0°C. After all the NH₄Cl has been added, the upper layer is removed as rapidly as possible and fractionated. The yield of trimethylchlorosilane is 85% of the theoretical.

HBr is a weaker halogenating agent, and in addition is slightly oxidized under the action of concentrated sulfuric acid. It is therefore advisable to effect the reverse transition from hexamethyldisiloxane to trimethylbromosilane under the action of phosphorus tribromide instead (Bibl.147).

Preparation of Trimethylbromosilane from Hexamethyldisiloxane. In a hermetically sealed vessel 163 g of hexamethyldisiloxane, 459 g of phosphorus tribromide, and 1 g of ferric chloride are mixed. The mixture is allowed to stand for 20 hours, and is then fractionated. The trimethylbromosilane passes over at 79.9°C (754 mm). The yield is 73% of theoretical.

Hexaethyldisiloxane is formed on hydrolysis of triethylhalosilanes (Bibl.148, 149), in the presence of the acid formed during the reaction:

\[
2(\text{C}_3\text{H}_9\text{SiCl}) + \text{H}_2\text{O} \rightarrow (\text{C}_3\text{H}_9\text{SiOSi(C}_3\text{H}_9\text{)S}_2 + 2\text{HCl}
\]

Hexaethyldisiloxane is a mobile liquid, boiling point 233°C, insoluble in water, which readily reacts with HCl to form triethylchlorosilane:

\[
(\text{C}_3\text{H}_9\text{SiOSi(C}_3\text{H}_9\text{)S}_2 + \text{H}_2\text{SO}_4 + 2\text{NH}_4\text{Cl} \rightarrow 2(\text{C}_3\text{H}_9\text{SiCl}) + (\text{NH}_4\text{})_2\text{SO}_4 + \text{H}_2\text{O}
\]

Preparation of Triethylchlorosilane from Hexaethyldisiloxane. To 275 ml of cold concentrated sulfuric acid, 265 g of hexaethyldisiloxane is added. Then 175 g of ammonium chloride is added over a period of 2 hours, with stirring, to the mixture so obtained. The mixture is stirred for another hour; then the upper layer is separated from the sulfuric acid and fractionated. The triethylchlorosilane passes over at 114°C (735 mm). The yield is 86% of theoretical (Bibl.149).

The reaction of hydrolysis of trialkylhalosilanes takes place with the formation of trialkylsilanols, at first, and then of hexaalkyldisiloxanes:
Depending on the character of the organic radical, and also on reaction conditions—the acidity of the medium, the temperature, the concentration of by products—the equilibrium may be shifted toward either side.

Triethylchlorosilanes, in contrast to trimethylchlorosilanes, is not hydrolyzed under the action of fuming HCl. On hydrolysis of trialkylhalosilanes in a neutral or alkaline medium under proper conditions (low temperature, presence of a solvent), an appreciable quantity of trialkylsilanols is formed, whose yield rises with increasing size of the organic radical attached to the silicon atom.

On the hydrolysis of trimethylchlorosilane by an aqueous solution of ammonia, hexamethyldisiloxane is the principal product. Tripropylbromosilane (Bibl.150,151), under these conditions forms a mixture of tripropylsilanol and hexapropyldisiloxane, while the principal reaction products in the hydrolysis of tributylchlorosilane or triisooamylobromosilane are the corresponding trialkylsilanols (Bibl.152, 153).

Tricyclohexylchlorosilane, \((C_6H_{11})_3SiCl\), in contrast to the other trialkylchlorosilanes, is not hydrolyzed by water or dilute HCl. Its hydrolysis may be accomplished by the action of a boiling alcoholic solution of caustic potash. The only product of the reaction will be tricyclohexylsilanol, and no disiloxane will be formed.

The low reactivity of tricyclohexylchlorosilane is probably due to steric hindrance due to the presence of three cyclohexyl groups attached to a single silicon atom (Bibl.154). Mixed trialkyl-(aryl)-halosilanes containing aromatic radicals, on hydrolysis in an acid medium, form silanols, which spontaneously undergo condensation on standing, and also under the action of dehydrating agents or of strong acids (HCl dissolved in glacial acetic acid, HNO_3, P_2O_5, ZnCl_2, CH_3COCl etc) (Bibl.155). The velocity of hydrolysis of triarylhalosilanes depend on the concentration of hydroxyl ions. The hydrolysis of triphenylfluorosilane by a 50% solution of water in acetone proceeds in an alkaline medium approximately 10^6 times as fast as in an acid medium.
These data allow us to postulate that the process of hydrolysis of triphenylfluorosilane is connected with the formation of a complex containing a penta-covalent silicon atom:

\[ \text{H}_3\text{O} + \text{Si} - \text{R} \rightarrow \text{HO} - \text{Si} + \text{R} + \text{H} \]

The siloxane bond in hexaaryldisiloxane is easily disrupted under the action of boiling alcoholic solutions of caustic potash, forming triarylsilanolates, which on acidification form silanols, which then undergo condensation of disiloxanes:

\[
\begin{align*}
(C_6\text{H}_{5})_3\text{SiOSi}(C_6\text{H}_{5})_3 + 2\text{KOH} & \rightarrow 2(C_6\text{H}_{5})_3\text{SiOK} + \text{H}_2\text{O} \\
2(C_6\text{H}_{5})_3\text{SiOK} + 2\text{HCl} & \rightarrow 2\text{KCl} + 2(C_6\text{H}_{5})_3\text{SiOH} \rightarrow (C_6\text{H}_{5})_3\text{SiOSi}(C_6\text{H}_{5})_3 + \text{H}_2\text{O}
\end{align*}
\]

Hexaalkyldisiloxanes are liquids, hexaaryldisiloxanes are crystalline substances readily soluble in organic solvents. The hexaalkyldisiloxanes are stable at high temperatures, and can be distilled under atmospheric pressure without decomposition. They are also stable against the action of alkalies, but when heated with an aqueous solution of NaOH under pressure, they are decomposed with the formation of methane and sodium silicate.

\[
(C_6\text{H}_{5})_3\text{SiOSi}(\text{CH}_3)_3 + 4\text{NaOH} \rightarrow \text{H}_2\text{O} \rightarrow 2\text{Na}_2\text{SiO}_3 + 6\text{CH}_4
\]

**Preparation of Sodium Silicate.** In 500 ml of a solution of NaOH, 0.5 mol of hexamethyldisiloxane is dissolved. The solution so prepared is heated in an autoclave at 200°C. The yield of methane is 76% of theoretical.

When hexaalkyldisiloxanes are dissolved in concentrated sulfuric acid, the siloxane bond is broken and an ester of sulfuric acid is formed: hexaalkylsulfonodisiloxane:

\[
(C_6\text{H}_{5})_3\text{SiOSi}(C_6\text{H}_{5})_3 + \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + (C_6\text{H}_{5})_3\text{SiOSO}_2\text{OSi}(C_6\text{H}_{5})_3
\]
Preparation of Hexaalkylsulfonodioxydisilane. A mixture of 99 g of hexaethyl-disiloxane and 56 g of 20% oleum is stirred at room temperature for 30 minutes. Then 40 g of ammonium sulfate is added to the mixture, and it is again stirred at room temperature for 2 hours. The hexaethylsulfonodioxysilane is extracted by pentane from the reaction mass, the pentane is distilled off, and the residue is distilled under reduced pressure. The hexaethylsulfonodioxysilane has a boiling point of 170°C (12 mm). It is partially decomposed on distillation (Bibl.112).

It was thought at first that this reaction leads at once to the formation of neutral esters of sulfuric acid. Later investigations, however, showed that the principal reaction product is trimethylsilane sulfate:

\[
2(CH_3)_3SiOSi(CH_3)_3 + 3H_2SO_4 \rightarrow 2(CH_3)_3SiOSO_3H + H_2O + (HSO_4)^- + (CH_3)_3SiOSi(CH_3)_3
\]

Together with the trimethylsilane sulfate a small amount of hexamethylsulfonodioxydisilane is also formed, and is extracted by pentane from the reaction mass. Owing to the removal of this substance by pentane, the equilibrium state is always being shifted toward the side of its formation, and thus the trimethylsulfonosilane gradually passes over into hexamethylsulfonodioxydisilane (Bibl.157).

Hexaalkyldisiloxanes containing functional groups in the organic radicals may be prepared by hydrolysis of the corresponding trialkylchlorosilanes. On the co-hydrolysis of dimethylchloromethylchlorosilane and trimethylchlorosilane, pentamethylchloromethyltrisiloxane is formed (Bibl.158):

\[
(CH_3)_3SiCl + (CH_3)C(CH_3)SiCl_3 + H_2O \rightarrow (CH_3)_3Si-O-Si(CH_3)_3 + 2HCl
\]

Preparation of Pentamethylchloromethyltrisiloxane. A mixture of 0.79 mol of dimethylchloromethylchlorosilane and 0.79 mol of trimethylchlorosilane is gradually added to 500 ml of water. The oil liberated is separated from the water layer.
dried over anhydrous sodium carbonate, and fractionated. The pentamethylchloromethyldisiloxane passes over at 151.6-151.8°C.

In this reaction hexamethyldisiloxane and 1,2-bis(chloromethyl)-tetramethyldisiloxane are simultaneously formed:

\[
2(CH_3)_5SiCl + H_2O \rightarrow (CH_3)_5SiOSi(CH_3)_4 + 2HCl \\
2(CH_3)_5CH2ClSiCl + H_2O \rightarrow (CH_3)_5CH2ClSiOSi(CH_3)_4 + 2HCl
\]

1,2-bis-(chloromethyl)-tetramethyldisiloxane (Bibl. 160, 161) distills at 201.4-204.5°C.

It is interesting to note that this compound cannot be obtained by direct chlorination of hexamethyldisiloxane, since the "Cl liberated as a result of the chlorination forms an equilibrium system with the hexamethyldisiloxane (Bibl. 156):

\[
(CH_3)_5SiOSi(CH_3)_4 + 2HCl \rightleftharpoons H_2O + 2(CH_3)_5SiCl
\]

The chlorinated derivatives of hexamethyldisiloxane easily split off methyl chloride when heated with an alcoholic solution of alkali. Even so weak a base as a 10% solution of potassium carbonate in butanol, after 11 minutes boiling with the corresponding chlorinated derivatives, causes cleavage of 80-90% of their chloromethyl groups.

\[
(CH_3)_5SiOSi(CH_3)_4CHCl + H_2O \rightarrow (CH_3)_5SiOSi(CH_3)_4OH + CH_3Cl \\
(CH_3)_5CH2ClSiOSi(CH_3)_4CHCl + 2H_2O \rightarrow HO(CH_3)_5SiOSi(CH_3)_4OH + 3CH_3Cl
\]

The hydroxysiloxanes so formed undergo condensation under the conditions of the reaction, thus forming polymeric products.

**Hydrolysis of Bifunctional Compounds**

In the hydrolysis of dialkylchlorosilanes, the initial reaction products are dialkylsilanediols.

The process of condensation of the initial hydrolysis products into polymeric
compounds still remains incompletely studied.

According to my own researches, the hydrolysis and condensation of the alkyl-substituted esters of orthosilicic acid, as well as of alkyl- and arylchlorosilanes (Bibl.139) with insufficient water, in a neutral medium, proceeds along the type of a reaction of stepwise condensation. In an excess of water, and in an acid medium, however (as shown by recent investigations), the process of formation of polyorganosiloxanes may take place not only according to the pattern of the condensation reaction, but also according to the pattern of polymerization reactions. This hypothesis is based on the results of a study of the processes of formation of polydimethylsiloxane elastomers from dimethyldichlorosilane. In these studies, I, in collaboration with N.K. Sokolov, succeeded, by mass-spectrometric analysis, in establishing the existence of a substance (Bibl.140) which is formed in considerable amounts both on formation and degradation of the polymers, namely dimethylsilicone:

\[
\begin{align*}
\text{CH}_3 & \quad \text{Si} = \text{O} \\
\text{CH}_3 &
\end{align*}
\]

Consequently, polyorganosiloxanes in acid media may be formed not only as a result of stepwise condensation, but simultaneously as a result of the polymerization of the alkylsilicone molecules that are formed. The predominance of one reaction or the other in the preparation of polyorganosiloxanes depends on the reagents taken in the reaction, and on the process conditions. The polymerization reaction probably predominates with the dialkylsilanediols, while the reaction of polymerization into rings and their condensation is probably dominant with the alkyl- and arylsilane-triols.

Since the molecules of the dialkylsilanediols and dialkylsilicones have two reactive centers, the process of condensation and polymerization may proceed in two directions, with the formation of linear (I) or cyclic (II) polymeric compounds.
The ease of formation of cyclic compounds on condensation of the products of the di-
alkyldichlorosilanes is a characteristic feature of these compounds. While in or-
ganic chemistry, the five- and six- membered carbon rings are the most stable, in a
number of organosilicon cyclic polymers, the eight- membered ring is apparently the
most stable.

In the six-membered ring

there are apparently considerable stresses. This is confirmed by the fact that under
the same reaction conditions the yield of polydimethylsiloxanes with six-membered
rings is always lower than with eight-membered rings.

A large number of papers have been devoted to the formation of the carbon rings
(Bibl.162). The original researches in this field led to the erroneous assertion
that only five- and six-membered rings could exist. Subsequent research showed the
possibility of obtaining rings with 15-20 carbon atoms in the ring.

Carothers and Hill (Bibl.163), studying the process of formation of cyclic poly-
esters from dicarboxylic acids and dihydric alcohols, came to the conclusion that the
introduction of an oxygen atom into a carbon ring is a means of reducing the stresses
in a cyclic compound.
The experience that has accumulated in investigating the processes of formation of the carbon ring can be utilized in studying the chemistry of the cyclic organo-silicon compounds. It should at the same time be noted that the theory of stresses is applicable only to planar rings, such as, for example, the ring of benzene or of hexamethylcyclotrisiloxane. The data obtained by X-ray diffraction studies of the polysiloxanes show that the sixteen-membered ring of the octamer \([(CH_3)_2SiO]_8\) is not of planar structure (Bibl.164). It must be concluded from this that the geometrically calculated value of the valence angle in the ring is not the only factor determining the ease or difficulty of ring closure.

A paper by A.Ye.Favorskiy (Bibl.165) devoted to the reversibility of the processes of isomerization, is very interesting. In this work the author considers the process of formation of cyclic compounds from the point of view of chemical thermodynamics. It is well known that the transition of less stressed rings into more stressed rings is observed in practice, although this is in direct contradiction with the theory of stress. From the thermodynamics of chemical reactions, however, it is well known that every reversible chemical system, under certain conditions, for example, under the introduction of energy from outside, may be converted into a system with a large supply of free energy. Thus the possibility of the formation of more highly stressed rings depends mainly on the conditions under which the reaction is conducted (Bibl.166). S.S.Nametkin (Bibl.167) states that the processes of formation on stressed rings usually takes place under the conditions of high temperatures, or pressures, or under high vacuum or when powerful chemical reagents or catalysts are used. Under these conditions, the stress in the ring as the factor controlling the process is not of decisive significance. The above propositions are well confirmed by the example of the cyclic organosilicon polymers. Thus, for instance, on the hydrolysis of dimethyldichlorosilane in an acid medium, the main reaction products are cyclic polymers of the composition \([(CH_3)_2SiO]_n\) (with values of \(n\) from 3 to 9), while the yield of the cyclic tetramer is maximum, amounting to 42% of theoretical.
Under these conditions the cyclic trimer is formed in the quantity of 0.5%. In case
the cyclic polymers are formed by thermal depolymerization of linear polydimethyl-
siloxane, the opposite picture is observed in vacuo. In this reaction the yield of
the cyclic trimer is 44% while the yield of tetramer falls to 24%. On the hydrolysis
of diethyl dichlorosilane in an acid medium, cyclic polymers are formed, consisting
mainly of tetramer. An alkaline medium during hydrolysis favors the formation of
linear polymers. This may be explained by the fact that on the condensation of di-
alkylsilanediols in a weakly alkaline medium, formation of an equilibrium system of
the type:

\[
\text{HO-Si-O-Si-OH} + \text{NaOH} \rightleftharpoons \text{NaO-Si-O-Si-OH} + \text{H}_2\text{O}
\]

is possible. The hydroxysilanolate structure (III) has the possibility of growth
primarily in one direction, owing to the blocking of one of the two hydroxyl groups
by a sodium ion. For this reason the formation of cyclic compounds is hindered. But
the disruption of the siloxane bond under the conditions of weakly alkaline hydroly-
sis under the action of a dilute aqueous solution of caustic soda is impossible.
Nevertheless, in consequence of the reversibility of this reaction, a certain quantity
of cyclic compounds (about 20%) is formed even on hydrolysis in the presence of an
alkali. Besides this, polymers containing hydroxyl groups are also present in the
products of hydrolysis of dialkyldichlorosilanes. This is confirmed by the fact that
a certain quantity of water is always liberated on the distillation of the polymers.
Its formation can be explained only by the further condensation of the dihydroxypoly-
dialkylsiloxanes:

\[
2\text{HO-Si-O-Si-OH} \rightleftharpoons \text{HO-Si-O-Si-OH} + \text{H}_2\text{O}
\]
The tendency of linear dihydroxyldiarylsiloxanes to undergo further condensation is determined by the elementary groups in the polymer (x). In this case, the greater the number x, the smaller the tendency of the polymer to further condensation.

If the process of condensation of dialkylsilane diols proceeds in a concentrated medium, where the frequency of mutual collisions between molecules is higher than the velocity of intramolecular ring closure, then the condensation is directed toward the side of the formation of linear high-molecular polymers. In the case of condensation in dilute solutions, where the possibility of the collision between the individual molecules is reduced, the process of formation of cyclic polymers is dominant. However, the presence of active solvents, which also block some of the hydroxyl groups, may direct the process of condensation toward the formation of linear compounds, for example, according to the mechanism:

\[
R_2SiCl_2 + C_2H_5OH \rightarrow R_2Si(OCH_2) + HCl
\]

\[
2R_2Si(OC_2H_5) + H_2O \rightarrow (C_2H_5OSiR_2(OCH_2)) + 2HCl
\]

The further hydrolysis of tetraalkyl dibutoxydisiloxane leads to the formation mainly of linear polymers.

The partial hydrolysis of dialkyl dichlorosilanes likewise leads to the formation of polymers of the linear structure:

\[
\begin{array}{c}
\text{R} \\
\text{Cl} \\
\text{Si} \\
\text{O} \\
\text{Si} \\
\text{Cl} \\
\text{R} \\
\text{R} \\
\end{array}
\]

The formation of dichloropropoxydialkyldichlorosiloxanes is favored by a homogenous medium during hydrolysis, and by the slow introduction of water into the solution of the dialkyl dichlorosilane. The primary products of the hydrolysis of the dialkyl dichlorosilane may be converted into high-polymer substances by means of subsequent heating.
Under these conditions, the increase in polymer chains length takes place on account of the condensation of the individual molecules at the hydroxyl end-groups:

During the process of condensation, the concentration of hydroxyl groups continuously falls. The rate of reaction also falls accordingly. The water liberated by the condensation reaction likewise slows the course of the reaction.

To accelerate the process of condensation, it is usually conducted at temperatures of 150-200°C, and a stream of inert gas is blown, at the same time, through the reaction mass to facilitate the removal of the water formed. For this same reason, most compounds able to bind the water set free during the condensation also encourage the acceleration of the process of condensation of organosilicon polymers. Such compounds are sulfuric acid, anhydrous halides of iron, antimony, or tin, sodium sulfate, triethanolamine, and esters of boric acid. Benzoyl peroxide and other oxidants (Bibl. 190) react by another mechanism.

The acceleration of condensation under the action of catalysts is caused by processes which may be divided into four main groups:

1. The condensation itself, leading to the formation of siloxane bonds between two Si-OH groups. Dehydrating agents catalyze this process.

2. Heteropolycondensation, accompanied by cocondensation between a substance with a considerable number of hydroxyl groups (H₂BO₃), and the hydroxyl groups of the organosilicon polymer by the reaction:

\[
\text{-Si-OH + H(OH)}_n + \text{HO-Si- -Si-O-B-O-Si- + 2H}_2\text{O}
\]
3. Degradative condensation, taking place as a result of the cleavage of organic radicals and the formation of an additional siloxane bond under the action of oxidants, such as benzoyl peroxide, oxygen, air at elevated temperatures, etc.

4. Rearrangement, accompanied by cleavage of the cyclic compounds and their conversion into linear high-polymers (under the action of sulfuric and chloric acid*, antimony pentachloride, alkali).

In practice, for the better conduct of the process of formation of the polymer molecule, the two latter methods are most often used, blowing air through the polymer or treating the hydrolysis product with alkaline or acids. When the polymeric products are treated with a stream of air at an elevated temperature, the partial cleavage of the organic radicals attached to the silicon atom is observed. This reaction is specific for polymers with aliphatic and certain other radicals. As a result of the reactions, an aldehyde is formed, according to the formula:

\[
4 \left( -\text{CH}_2R -\right) + 5\text{O}_2 \rightarrow 4 \left( -\text{Si}-\text{O} -\right) + 4\text{RCO}_2\text{H} + 2\text{H}_2\text{O}
\]

where \( R \) is a hydrocarbon radical or a hydrogen atom.

At the place of the cleaved organic radicals an additional siloxane bond, joining the linear molecules by a transverse bridge, appears. By blowing air through the polymer, the low-molecular cyclic products may also be condensed. The structure of the polymer formed in this case is expressed by the following formula:

\[
\begin{align*}
\text{R} & \text{Si}-\text{O} -\text{Si}-\text{O} -\text{Si} -\text{O} -\text{Si} -\text{O} -\text{Si} -\text{O} -\text{Si} \\
& \text{R} \text{R} \text{R} \text{R} \\
\end{align*}
\]

* As in text-Translator.
Cyclic low-polymer polyorganosiloxanes, in my opinion, are best of all converted into linear polymers of higher molecular weight, by acting on the cyclic compounds with dry or concentrated alkali and using dry HCl or aqueous solutions of acids to neutralize it. In this case the maximum weight of the polymer molecules is obtained. For organosilicon polymers with aromatic groups, it is characteristic that when a stream of moist air is blown through the polymer in the presence of catalytic quantities of HCl, the cleavage of the phenyl groups and formation of benzene is observed:

\[
\begin{align*}
\text{C}_\text{n} \text{H}_\text{n} & \quad \text{+} \quad \text{H}_\text{2} \text{O} \quad \text{→} \quad \text{HO-Si-CH}_\text{3} \quad \text{+} \quad \text{C}_\text{n} \text{H}_\text{n} \\
\text{HO} & \quad \text{+} \quad \text{Si} \quad \text{+} \quad \text{H}_\text{2} \text{O} \quad \text{→} \quad \text{H}_\text{2} \text{O} \quad \text{+} \quad \text{Si} \quad \text{+} \quad \text{C}_\text{n} \text{H}_\text{n}
\end{align*}
\]

The cleavage of the aromatic group under the action of HCl is accompanied by the formation of an Si-Cl bond.

\[
\text{Si-Cl} + \text{H}_\text{2} \text{O} \quad \text{→} \quad \text{Si} \quad \text{+} \quad \text{H}_\text{2} \text{O} \quad \text{+} \quad \text{Cl}_\text{2}
\]

The Si-Cl bond so formed is readily hydrolyzed by moist air:

\[
\text{Si} \quad \text{+} \quad \text{H}_\text{2} \text{O} \quad \text{→} \quad \text{Si} \quad \text{+} \quad \text{OH} \quad \text{+} \quad \text{HCl}
\]

The HCl is continuously regenerated, and is thus the catalyst of the process.

The first representatives of the class of bifunctional compounds, dimethyldichlorosilane, reacts energetically with water to form HCl and polymeric cyclic and linear products:

\[
\text{(n+1)H}_\text{2} \text{O} \quad \text{+} \quad \text{[(CH}_3\text{)}_2\text{SiCl}_3]_\text{n} \quad \text{→} \quad \text{[(CH}_3\text{)}_2\text{SiO}]_\text{n} \quad \text{+} \quad \text{2nHCl}
\]

Hydrolysis of Dimethyldichlorosilane in Water. To 12000 g of water, under vigorous stirring, 4250 g of dimethyldichlorosilane is gradually added. The temperature
of the mixture during the process of addition of the dimethyldichlorosilane is held within the limits of 15-20°C. The oily upper layer is separated from the water layer washed free of HCl, and the low-boiling cyclic compounds are distilled off, at first under atmospheric pressure (up to 175°C), and then under the reduced pressure of 20 mm. The yield of the distilled fraction is 50.8% of the weight of the hydrolysis product of dimethyldichlorosilane. This fraction is a mixture of the cyclic trimer, tetramer, pentamer, and hexamer, whose yield, in % of theoretical, amounts to:

\[
\begin{align*}
[(\text{CH}_3\text{SiO})_3] & \quad \cdots \quad 0.5\% \\
[(\text{CH}_3\text{SiO})_4] & \quad \cdots \quad 6.7\% \\
[(\text{CH}_3\text{SiO})_6] & \quad \cdots \quad 42\% \\
[(\text{CH}_3\text{SiO})_9] & \quad \cdots \quad 1.6\%
\end{align*}
\]

The remaining 49.2% consists of the undistilled retort residue, from which small amounts of cyclic heptamer, octamer, and nonamer may be separated. It is also possible that the retort residue, after the highest boiling cyclic compound the nonamer, \([(\text{CH}_3)_2\text{SiO})_9], has been distilled off, contain still higher-molecular cyclic compounds, which cannot be separated even by fractional distillation under a high vacuum (Bibl.180).

On hydrolysis of dimethyldichlorosilane in ether solution, under the conditions of a strongly acid medium, the yields of low-molecular products amount to 95-98% of the weight of the hydrolysis product.

**Hydrolysis of Dimethyldichlorosilane in Ether.** In 400 ml of ether 250 g of dimethyldichlorosilane is dissolved. The solution is slowly poured, with vigorous stirring, into 400 ml of water. The temperature is held within the range 10-20°C during the entire process of hydrolysis. The maximum concentration of the HCl liberated is about 6 mols per liter (20%), under the condition of the uniform distribution of the HCl between the water and the ether. The organic layer is separated and washed with water until its reaction is neutral. The ether is then distilled off. The product of the hydrolysis consists of 98% of cyclic compounds passing over in vacuo (under 1 mm pressure and maximum temperature 200°C), and containing 3 to 7
silicon atoms in the chain.

On partial hydrolysis of dimethyldichlorosilane, dichloropolydimethylsiloxanes are formed:

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_2 & \quad \text{CH}_3 \\
\text{Cl-Si(O)-Si(Cl)} & \quad \text{Si-O-Cl} & \quad \text{Si-Cl}
\end{align*}
\]

It is advisable to conduct this reaction in the presence of a solvent in which water and dimethyldichlorosilane are equally soluble. Dioxane is a suitable solvent for this purpose.

**Hydrolysis of Dimethyldichlorosilane in Dioxane.** In 2000 ml of ether 16.6 mols of dimethyldichlorosilane is dissolved. A solution of 8.3 mls of water in 150 ml of dioxane is slowly added to this solution, with vigorous stirring and under external cooling. During the reaction, gaseous HCl is evolved, which to some extent, entrains the vapor of dimethyldichlorosilane and of the solvent. To prevent the volatilization of the products, the reaction flask is connected with a reflux condenser cooled with a solution of solid carbon dioxide in acetone (Bibl.168).

After the hydrolysis has been completed, the reaction mixture is fractionated. The composition of the mixture of hydrolysis products, in %, is as follows:

<table>
<thead>
<tr>
<th>Compound</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unreacted ((\text{CH}_3)_2\text{SiCl}_2)</td>
<td>22</td>
</tr>
<tr>
<td>(\text{Cl(\text{CH}_3)_2SiOSi(\text{CH}_3)_2\text{Cl}})</td>
<td>28</td>
</tr>
<tr>
<td>(\text{Cl(\text{CH}_3)_2SiOSi(\text{CH}_3)_2OSi(\text{CH}_3)_2\text{Cl}})</td>
<td>24</td>
</tr>
<tr>
<td>(\text{Cl(\text{CH}_3)_2Si[OSi(\text{CH}_3)_2\text{OSi(\text{CH}_3)_2\text{Cl}})}</td>
<td>15</td>
</tr>
<tr>
<td>(\text{Cl(\text{CH}_3)_2Si[OSi(\text{CH}_3)_2\text{OSi(\text{CH}_3)_2\text{Cl}})}</td>
<td>6</td>
</tr>
<tr>
<td>(\text{Cl(\text{CH}_3)_2Si[OSi(\text{CH}_3)_2\text{OSi(\text{CH}_3)_2\text{Cl}})}</td>
<td>3</td>
</tr>
<tr>
<td>Undistilled Residue</td>
<td>2</td>
</tr>
</tbody>
</table>

If the partial hydrolysis of dimethyldichlorosilane is conducted in the absence of a solvent, the composition of the hydrolysis product is sharply different, and the yield of linear dichloropolydimethylsiloxanes is considerably lower. At the same
time, the cyclic tetramer and pentamer, as well as a large amount of undistilled residue, may be detected among the hydrolysis products. In this case, the composition of the mixture of reaction products, in %, is as follows:

<table>
<thead>
<tr>
<th>Compound</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unreacted ((\text{CH}_3)_2\text{SiCl}_2)</td>
<td>62</td>
</tr>
<tr>
<td>(\text{Cl(\text{CH}_3)_2SiOSi(\text{CH}_3)_2\text{Cl}})</td>
<td>6</td>
</tr>
<tr>
<td>(\text{Cl(\text{CH}_3)_2SiOSi(\text{CH}_3)_2\text{SiOSi(\text{CH}_3}_2\text{Cl}})</td>
<td>2</td>
</tr>
<tr>
<td>([\text{(CH}_3)_2\text{SiO}]_n)</td>
<td>11</td>
</tr>
<tr>
<td>([\text{(CH}_3)_2\text{SiO}]_5)</td>
<td>2</td>
</tr>
<tr>
<td>(\text{Cl(\text{CH}_3)_2Si[OSi(\text{CH}_3)_2\text{OSi(\text{CH}_3}_2\text{Cl}})</td>
<td>1</td>
</tr>
<tr>
<td>Undistilled Residue</td>
<td>16</td>
</tr>
</tbody>
</table>

These data show the process of partial hydrolysis of dimethyldichlorosilane in a homogenous medium to be stepwise in nature. In the first stage of the reaction, dimethylchlorosilanol is formed, which reacts with a molecule of dimethyldichlorosilane to form tetramethyldichlorodisiloxane:

\[
(\text{CH}_3)_2\text{SiCl}_2 + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_2\text{SiOH} + \text{HCl}
\]

\[
(\text{CH}_3)_2\text{SiOH} + \text{(CH}_3)_2\text{SiCl}_2 \rightarrow (\text{CH}_3)_4\text{SiOSi(\text{CH}_3}_2\text{Cl} + \text{HCl}
\]

The formation primarily of tetramethyldichlorodisiloxane is easy to explain theoretically by using the equation derived by us for the stepwise processes of hydrolysis and condensation of alkyl-substituted esters of orthosilicic acid (Bibl.169) (cf. page 270). In the case of partial hydrolysis of dimethyldimethylchlorosilane with a molar ratio of 8.3 : 16.6 between water and dimethyldichlorosilane, the degree of polymerization will be:

\[
A = \frac{n}{n-m} = \frac{16.6}{16.6-8.3} = 2
\]
and, consequently, tetramethyldichlorodisiloxane should be the principal reaction product. In heterogeneous hydrolysis, the process is not of stepwise nature, and as a result of the reaction, together with a larger amount of unreacted dimethyldichlorosilane, the mixture also contains up to 30% of completely hydrolyzed product.

The structure of hexadecamethylcyclooctasiloxane has been investigated by means of X-ray analysis. This substance forms transparent crystals, with the elementary cell of the crystal consisting of two molecules of \((\text{CH}_3)_2\text{SiO}_8\). Such a molecule has a symmetrical ring structure and is not planar. The crystals possess the piezoelectric effect, but are optically inactive (Bibl.170, 174).

A number of empirical formulas are known for the cyclic polydimethylsiloxanes, relating their physical properties with the number of silicon atoms in the ring.

Thus, for instance, the latent heat of vaporization (in kcal per mol) is expressed by the equation:

\[
H = 5.45 + 1.35x
\]  

where \(x\) = number of silicon atoms in the ring.

The vapor pressure is expressed by the equation:

\[
\lg P = 7.07 - \frac{1190}{T} + 0.265 - \frac{294}{T}x
\]

\(P\) = pressure, mm Hg;
\(T\) = absolute temperature, °C;
\(x\) = number of silicon atoms in ring.

There is an empirical equation relating the viscosity of cyclic polydimethylsiloxanes with the molecular weight:

\[
\lg \eta = -1.44 + 2.74 \lg x
\]

where \(\eta\) = viscosity in centipoises at 38°C;

\(x\) = number of silicon atoms in ring.

The relation of the viscosity to the temperature may be expressed by means of
the Arrhenius equation in the following form:

$$\eta = Ae^{\frac{E}{RT}}$$

(4)

where $E =$ energy of activation of viscous flow.

Since the energy of activation of viscous flow is a linear function of the logarithm of the number of silicon atoms in the polymer, and is expressed for cyclic polydimethylsiloxane by the equation

$$E = 0.98 + 3.96\lg x$$

(5)

then, starting out from eqs. (3), (4), and (5), the general equation for the viscosity of cyclic polydimethylsiloxanes over the range of temperatures from 38 to 100°C may be derived:

$$\lg \eta = -2.13 + \frac{214}{T} - \left[0.04 - \frac{866}{T}\right]\lg x$$

The slight variation of the viscosity with the temperature is a confirmation of the weak associative forces between the molecules of cyclic polydimethylsiloxanes, and is of great practical importance, as well as considerable theoretical interest (cf. Chapter X).

The linear and cyclic polydimethylsiloxanes are chemically stable substances. The cyclic polymers (up to and including the hexamer) may be distilled under atmospheric pressure without appreciable signs of decomposition.

When linear polydimethylsiloxanes are heated to temperatures of 200-250°C, the liberation of water and the completion of the condensation process are observed, with the formation of higher-polymer products:

$$\overset{\text{CH}_3}{\text{CH}_2\text{Si(O-Si)}_x\text{OH}} \rightarrow \overset{\text{CH}_3}{\text{CH}_2\text{Si(O-Si)}_2\text{OH} + \text{H}_2\text{O}}$$

F-TS-9191/V
The esters of boric acid, triethanolamine, antimony pentachloride, and sulfuric acid are particularly effective accelerators of the process of polycondensation of the hydrolysis products of dimethyldichlorosilane (Bibl.171).

The hydrolysis product of dimethyldichlorosilane is mixed with half the amount of the ethyl ester of boric acid, and heated to 190°C. A solid polymer is formed in 10 minutes, while several hours are needed for the condensation, without a catalyst, to a similar state. The reaction of polymerization proceeds according to the following mechanism:

\[
\begin{align*}
2C_2H_5OH + \text{HOSi(CH}_3)_2\text{OSi(CH}_3)_2\text{OSi(CH}_3)_2\text{HOSi(CH}_3)_2\text{OSi(CH}_3)_2
\end{align*}
\]

\[
\begin{align*}
\text{B-OCH}_3
\end{align*}
\]

The excess of the boric acid ester remains dissolved in the polymer and has no effect on its final technological properties (Bibl.175).

When the hydrolysis products of dimethyldichlorosilane are treated with a stream of air at an elevated temperature, together with condensation at the hydroxyl groups, cleavage of the organic radicals also occurs, forming the corresponding aldehyde. The number of oxidized methyl groups is small and depends on the rate of passage of the gas, the temperature, the oxygen concentration, and the presence of foreign substances. Thus, for example, analysis of a specimen (prepared by heating the product of hydrolysis of dimethyldichlorosilane at 200°C until it had been converted into an elastic rubberlike product) showed (Bibl.177) it to contain 82.5% of silicon dioxide instead of the theoretical amount of 81.8%.

According to the analytical data, this polymer has the formula \((\text{CH}_3)_1.82\text{SiO}_{1.09}\) instead of the theoretical formula \((\text{CH}_3)_2\text{SiO}_2\), and, consequently, the loss of methyl groups amounts to about 0.18 \(\text{CH}_3\) per hundred silicon atoms (Bibl.172).

The literature also gives descriptions of studies devoted to the elucidation of the relation of the number of methyl groups cleaved with the composition of the gas.
passed through and with the presence of foreign substances (Bibl.191). Through weighed portions of polydimethylsiloxane polymer (25 g) at 200°C, streams of various gases were passed for 168 hours at the rate of 20 ml/min. The formaldehyde and formic acid formed were caught by titration with an alkali solution, and their content was determined by the bisulfite method, or by means of hydroxylamine hydrochloride. The starting polymer taken for the experiment had a viscosity of 72.4 centistokes. The change of viscosity of the polymer at the end of the process, and the number of methyl groups undergoing cleavage was as follows:

<table>
<thead>
<tr>
<th>Gas</th>
<th>Viscosity after Condensation, in Centistokes</th>
<th>Number of CH₃ Groups Cleaved, Per 100 Silicon Atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Helium (Not over 0.1% of O₂)</td>
<td>76.2</td>
<td>0.07</td>
</tr>
<tr>
<td>Nitrogen (0.5% of O₂)</td>
<td>83.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Air</td>
<td>107</td>
<td>1.26</td>
</tr>
<tr>
<td>Oxygen</td>
<td>120</td>
<td>1.92</td>
</tr>
</tbody>
</table>

The presence of certain metals affects the oxidation of organic radicals in polydimethylsiloxanes. Of the metals investigated, copper, selenium, and lead are inhibitors of the process of oxidation. Tellurium, to a slight extent, accelerates oxidation of the methyl groups in polydimethylsloxanes; silver, cadmium, zinc, iron, steel, and duralumin have no effect on the process of oxidation. The reaction was conducted under the conditions described above, with the single difference that turnings of the metal, 31 x 6 x 0.8 mm in size, were introduced into the polymer. The original polymer was the same.

The change in the viscosity of the polymer, and the number of metal groups cleaved per 100 silicon atoms during the process of oxidation of polymers in the presence of certain elements, are given in Table 64.
Influence of Metals on Oxidation of Polydimethylsiloxanes

<table>
<thead>
<tr>
<th>Gas</th>
<th>Copper</th>
<th>Selenium</th>
<th>Lead</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Viscosity of Polymer (Centistokes)</td>
<td>Number of CH₃ Groups Cleaved Per 100 Silicon Atoms</td>
<td>Viscosity of Polymer (Centistokes)</td>
</tr>
<tr>
<td>Air</td>
<td>80.5</td>
<td>0.3</td>
<td>77.7</td>
</tr>
<tr>
<td>Oxygen</td>
<td>80.2</td>
<td>0.26</td>
<td>76.6</td>
</tr>
</tbody>
</table>

Our attention is drawn by the data on the increase in the viscosity of the polymer on oxidation in the presence of lead. At the same time, in the presence of lead, a considerable loss in weight is observed, owing to the volatilization of the low-molecular products. Since the starting polymer does not contain low-molecular impurities, their formation during the process of condensation must be attributed to the influence of the lead. The lead during the process of oxidation also undergoes changes. The shining surface of the metal is gradually covered by a gray film, the liquid becomes turbid, and, toward the end of the oxidation, a precipitate accumulates on the bottom of the reaction flask.

It is well known that lead oxide reacts with trimethylsilanol to form lead bis-trimethylsilanolate:

$$2(CH₃)₃SiOH + PbO - H₂O + [(CH₃)₂SiO]₂Pb$$

Patnode and Schmidt postulate that the lead oxide might also disrupt the polysiloxane chains according to the scheme:
The derivatives of lead, under the conditions of elevated temperatures, may undergo rearrangement to form either linear or cyclic compounds. If a cyclic polymer is formed, however, it will be removed from the system, since it is more volatile than the linear polymers, and in this way the reaction will shift towards the side of formation of cyclic compounds: at higher temperatures the rate of oxidation of the radicals appreciably rises. In this case an insoluble three-dimensional polymer will be formed and gelation will take place. Thus, for instance, at 225°C, the gelation of the same starting polymer (of viscosity 72.4 centistokes) begins 24 hours after air or oxygen has been passed through under the above conditions. On the cold parts of the reaction flask a dense white precipitate of paraformaldehyde is deposited. We present data on the oxidation on the methyl groups in the polydimethylsiloxanes and on the influence of metals on the process of oxidation at 225°C:

<table>
<thead>
<tr>
<th>Gas</th>
<th>Time from Beginning of Condensation to Instant of Coagulation, Hours</th>
<th>Number of CH₃ Groups Cleaved Per 100 Silicon Atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>24</td>
<td>~ 2.5</td>
</tr>
<tr>
<td>Oxygen</td>
<td>24</td>
<td>~ 3.8</td>
</tr>
<tr>
<td>Air in the Presence of Copper</td>
<td>72-96</td>
<td>--</td>
</tr>
<tr>
<td>Air in the Presence of Selenium</td>
<td>Does not coagulate after 168 Hours</td>
<td>--</td>
</tr>
<tr>
<td>Air in the Presence of Lead</td>
<td>96-120</td>
<td>--</td>
</tr>
</tbody>
</table>

It will be seen from these data that at a high temperature, in the presence of
copper, selenium, or lead, the process of gelation is slowed.

In the presence of selenium, the losses due to volatilization during condensation amount to about 70%, while the viscosity of the condensed polymer is lower than that of the polymer in its original state. In the stripped volatile portion, hexamethylocyclotrisiloxane and octamethylcycloctetrasiloxane were found. The presence of selenium in the polymer leads to the rearrangement of linear polymers into cyclic; it is possible that the mechanism of the rearrangement in this case is the same as in presence of lead. At a temperature of 250°C, the oxidation proceeds still more vigorously. The aldehyde liberated in gaseous form is energetically oxidized to formic acid, or, at a high temperature, it is decomposed into CO and H₂. When a polymer is heated with its surface in contact with air, but without air being blown through it, the process of oxidation is sharply retarded and depends largely on such conditions as the relationship between the surface area of the polymer and its volume, the shape of the vessel, the temperature, etc.

On heating polymers not containing hydroxyl groups in sealed ampules for 168 hours at 250°C, practically no changes of their physical properties are observed. These data speak for the exceptional thermal stability of the polydimethylsiloxanes. When linear and cyclic polydimethylsiloxanes are heated with 3N solution of alkali, the methyl groups are cleaved, and methane and sodium silicate are formed:

\[
[(\text{CH}_3)\text{Si(O)}]_n + 2n\text{NaOH} \rightarrow n\text{Na}_2\text{SiO}_3 + 2n\text{CH}_4
\]

The yield methane is 77% of theoretical.

Polydimethylsiloxane containing functional groups in the organic radicals may be prepared by hydrolysis of the corresponding chloromethyl dichlorosilanes. Thus, for example, methylchloromethyl dichlorosilane, \((\text{CH}_3)(\text{CH}_2\text{Cl})\text{SiCl}_2\), is readily hydrolyzed by the action of water, forming oily polymeric products of the following structure (Bibl.189):

\[
\begin{array}{c}
\text{CH}_3 \quad \text{CH}_2\text{Cl} \quad \text{CH}_2\text{Cl} \\
\text{Si} \quad \text{Si} \quad \text{Si} \quad \text{Si} \\
\text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3
\end{array}
\]
On heating the polymer so obtained with solid caustic potash, the chloromethyl groups are cleaved, forming methyl chloride:

\[
\text{[(CH}_3\text{)(CH}_2\text{Cl)]_n + n\text{KOH} \rightarrow \text{CH}_3\text{SiOl}_n + n\text{CH}_3\text{Cl}}\]

The hydrolyzate of methyl(dichloromethyl)dichlorosilane, \((\text{CH}_3)(\text{CHCl}_2)\text{SiCl}_2\), is likewise stable against acid hydrolysis, but easily cleaves its chloromethyl groups under the action of a 10% aqueous solution of caustic potash:

\[
\text{CHCl}_3\text{CHCl}_3 \rightarrow \text{OH} \text{ OH} \rightarrow \text{CHCl}_3\text{H}_2\text{O} + 2\text{HCl} \rightarrow \text{CHCl}_3\text{H}_2\text{O} + 2\text{HCl}.
\]

Owing to the hydroxyl groups formed as a result of the cleavage of the chloromethyl groups, a polymer of the composition \((\text{CH}_3\text{SiOl}_{1.5})_n\) is formed.

The chloromethyl groups are partially cleaved from methyltrichloromethyl dichlorosilane, \((\text{CH}_3)(\text{CCl}_3)\text{SiCl}_2\), even on hydrolysis in an acid medium. Under the action of aqueous solutions of alkalies, the hydrolysis proceeds still more energetically:

\[
n(\text{CH}_3\text{CCl}_3\text{SiCl}_4) + 1.5n\text{H}_2\text{O} \rightarrow (\text{CH}_3\text{SiOl}_{1.5})_n + n\text{CHCl}_3 + 2n\text{HCl}.
\]

The methylchloromethylsiloxanes may be prepared by the chlorination of siloxane.

On the chlorination of octamethylcycloctetrasiloxane at 50-60°C under ultraviolet irradiation, heptamethylchloromethylcycloctetrasiloxane is formed (Bibl.172).

This substance is a liquid, melting point -10°C, boiling point 127°C (50 mm), specific gravity \(d_2^0 = 1.044\); refractive index \(n_2^0 = 1.4158\).
The product does not decompose on boiling with water or with the mixture of water and dioxane, but boiling with a 15% solution of caustic potash or potassium carbonate in butanol for 15 minutes leads to the cleavage of the chloromethyl group and the formation of a polymeric product of the following structure:

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{Si} & \quad \text{O} & \quad \text{Si} & \quad \text{O} & \quad \text{Si} & \quad \text{O} & \quad \text{Si} & \quad \text{H}_2\text{C} \\
\text{H}_2\text{C} & \quad \text{Si} & \quad \text{O} & \quad \text{Si} & \quad \text{O} & \quad \text{Si} & \quad \text{O} & \quad \text{Si} & \quad \text{H}_2\text{C} \\
\text{H}_2\text{C} & \quad \text{Si} & \quad \text{O} & \quad \text{Si} & \quad \text{O} & \quad \text{Si} & \quad \text{O} & \quad \text{Si} & \quad \text{H}_2\text{C}
\end{align*}
\]

The degree of completion of the reaction, according to the \(\text{CH}_3\text{Cl}\) liberated, is 88%. Simultaneously with the cleavage of the chloromethyl groups, the rearrangement of the polydimethylsiloxane structures under the action of alkali is observed.

With the object of studying the effect of sulfuric acid on polydimethylsiloxanes, the depression of the freezing point of solutions of polydimethylsiloxanes is concentrated sulfuric acid was investigated (Bibl.201).

It was found that the i-factor (the ratio of the observed freezing point depression to the calculated depression) strongly depends on the nature of the solute. Thus, for instance, the i-factor for hexamethyldisiloxane is 4.28, for octamethylcyclotetrasiloxane, it is 12.59, for \([(\text{CH}_2)_3\text{SiO}]_3\text{SiCH}_3\), it is 8.23 and for \([(\text{CH}_3)_3\text{SiO}]_4\text{Si}\) it amounts to 9.50. As stated above, the principal reaction when sulfuric acid acts on hexamethyldisiloxane takes place according to the following scheme:

\[
(\text{CH}_3)_3\text{SiOSi(CH}_3)_3 + 3\text{H}_2\text{SO}_4 \rightarrow 2(\text{CH}_3)_3\text{SiOSO}_2\text{OH} + \text{H}_2\text{O}^+ + \text{HSO}_4^-
\]

This would correspond to the i-factor = 4.00. The i-factor actually determined, however, was 4.28. A certain amount of increase in the value of the i-factor may be explained by the partial ionization of the \((\text{CH}_3)_3\text{SiOSO}_2\text{OH}\) group. If not the acid sulfate but the normal sulfate, \((\text{CH}_3)_3\text{SiOSO}_2\text{OSi(CH}_3)_3\), is formed, then the i-factor should equal 3, or it would have to be assumed that the reaction must take place
according to the following equation:

$$(\text{CH}_3)_3\text{SiOSO}_2\text{Si}(\text{CH}_3)_3 \cdots \cdot \text{Si}(\text{CH}_3)_3^+ + (\text{CH}_3)_3\text{SiOSO}_4^-$$.  

It is, however, improbable that any compounds other than acid sulfate could be formed in so strong an acid medium. It would be more correct to suppose that in the process of treating hexamethyldisiloxane with an excess of sulfuric acid, full sulfates are formed in small amounts, and that on extraction of the reaction mixture with pentane they pass into the organic layer, owing to their better solubility. As a result, the equilibrium is shifted, and a certain quantity of neutral sulfates is again formed in the reaction mixture. The somewhat higher value of the i-factor in the product obtained on the action of an excess of sulfuric acid on octamethylcyclotetrasiloxane (12.5 instead of the theoretical value of 12), may probably be explained by the ionization of the ester $\text{HHO}_2\text{SOSi}(\text{CH}_3)_2\text{OH}$, which is formed as a result of the reaction:

$$[\text{Si}(\text{CH}_3)_3\text{O}]_3 \cdot \text{Si}(\text{CH}_3)_2 \text{H}_2 \text{SO}_4 \rightarrow 4\text{HHO}_2\text{SOSi}(\text{CH}_3)_2\text{OSO}_2\text{OH} + 4\text{H}_3\text{O}^+ \cdot 4\text{HSO}_4^-$$

The deviation of the i-factor amounts on the average to 0.28 for $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$, and to 0.59 for $[(\text{CH}_3)_2\text{SiO}]_4$. But if the value of these deviations is recalculated for a single silicon atom, then we get practically the same figures. This shows that the dissociation of the compounds $(\text{CH}_3)_3\text{SiOSO}_2\text{OH}$ and $\text{HHO}_2\text{SOSi}(\text{CH}_3)_2\text{OSO}_2\text{OH}$ proceeds on approximately the same level, and that the degree of dissociation is small in absolute value. The theoretical value of the i-factor is 10 for $[(\text{CH}_3)_3\text{SiO}]_3\cdot \text{SiCH}_3$ and 13 for $[(\text{CH}_3)_2\text{SiO}]_4\cdot \text{Si}$. Since the experimentally observed values are considerably lower than these values, it must be assumed that polymerization processes take place in these cases. The reaction of $[(\text{CH}_3)_3\text{SiO}]_3\cdot \text{SiCH}_3$ with sulfuric acid may be expressed by this following equation, which corresponds to the observed values of the i-factor:
If the value of x in the first equation is sufficiently high, then the value of the i-factor is 7, while for the second equation the value of the i-factor is 8.5. Both reactions probably take place in reality.

When sulfuric acid reacts with the compound \([(\text{CH}_3)_3\text{SiO}]_4\text{Si}\), the following reactions may take place:

\[
[(\text{CH}_3)_3\text{SiO}]_4\text{Si} + 7.5\text{H}_2\text{SO}_4 \rightarrow 4(\text{CH}_3)_3\text{SiOSO}_4\text{OH} + 5\frac{1}{x} [\text{Si}_2(\text{OSO}_4\text{OH})_x\text{O}_y], + \frac{5}{2} \text{H}_2\text{O} + \frac{5}{2} \text{HSO}_4^{-}
\]

in which the i-factor for the first equation is 9 and for the second equation 10.

In the catalytic rearrangement of polydimethylsiloxane hydrolyzates, the amount of concentrated sulfuric acid used is about 5% the weight of the weight of the hydrolyzate.

On heating with sulfuric acid, most trimethylorganosilanes containing a functional group in the radical evolve methane (Bibl.173):

\[
\begin{align*}
\text{H}_3\text{SiCl(CH}_3\text{CHOH} + \text{H}_2\text{SO}_4 & \rightarrow \text{HOOCCCH}_3\text{Si}[(\text{CH}_3)_3\text{OSO}_4\text{H} + \text{CH}_4
\end{align*}
\]

On hydrolysis of diethyldichlorosilane, viscous oily products of partial condensation are formed. They are both of linear and cyclic structure (Bibl.190):
The formation of cyclic polymers, just as in the case of polydimethylsiloxanes, is favored by an acid medium and by the presence of an inactive solvent during hydrolysis.

**Hydrolysis of Diethyldichlorosilane.** 1. In 1.5 liter of water at 0°C, 260 g of dimethyldichlorosilane is introduced, with vigorous stirring. An oil is obtained which is separated from the water layer, and is then dissolved in ether. The ether solution is washed twice with water, and then dried over potassium carbonate. The ether is distilled off and the oil is fractionated. The yield of cyclic trimer and tetramer is 14.8% and 29.2% of the theoretical. A higher yield of cyclic polydiethyldiethylsiloxanes is obtained when ether is used as a solvent during the process of hydrolysis.

2. To a solution of 478 g of diethyldichlorosilane in 700 ml of ether, 478 g of ice is added. After all the ice has melted, the mixture is boiled under a reflux condenser for 1 hour, then the water layer is separated, and the ether layer is washed once with an equal volume of water. For the final hydrolysis and complete condensation, the organic layer is boiled with a 5% solution of NaOH for 1 hour. It is then washed with water until the reaction is neutral, and the ether is then distilled off. The polymer so obtained contains 62% of cyclic products, which are separated by distillation from the high-molecular compounds. The distillate so obtained contains 60-70% of cyclic trimer and 10-20% of cyclic tetramer, which are then separated in a rectification column with 20 theoretical plates, packed with glass rings. The rectification is conducted in vacuo. The physical properties of hexaethylcyclotrisiloxane and octaethylcyclotetrasiloxane are given on page 575.

The cyclic polydiethyldiethylsiloxanes are liquids insoluble in water, but readily soluble in ethers and aromatic hydrocarbons (Bibl.176).

On hydrolysis of diethyldichlorosilanes, the purity of the starting products has a substantial effect on the properties of the polymer obtained (Bibl.177).

Diethyldichlorosilanes of various degrees of purification was subjected to
hydrolysis. The relation between the molecular weight of the polymer obtained after hydrolysis (cryoscopically determined) on the degree of purification of the diethyl-dichlorosilanes, will be seen from the following data:

<table>
<thead>
<tr>
<th>Diethylidichlorosilane</th>
<th>Molecular Weight of Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled once</td>
<td>815</td>
</tr>
<tr>
<td>Distilled twice</td>
<td>600</td>
</tr>
<tr>
<td>Distilled three times</td>
<td>410</td>
</tr>
<tr>
<td>Recrystallized at -96.5°C</td>
<td>250</td>
</tr>
</tbody>
</table>

It will be seen from these data that the purer the starting diethylidichlorosilane, the lower the molecular weight of the polymer obtained from it. This may be explained by the presence, in the starting diethylidichlorosilane, of an admixture of ethyldichlorosilane, forming a higher-molecular branched polymer.

The effect of the purity of the starting diethylidichlorosilane on the viscosity and other properties of the polymer obtained by heating the polymer at 200°C, likewise confirms this hypothesis (Table 65).

As will be seen from these data, for a once purified diethylidichlorosilane, the slight change of viscosity by comparison with the change in the molecular weight is characteristic. This is evidence that the polymer formed is of branched structure, since, for equal molecular weights, the viscosity of a linear polymer is higher than that of a branched polymer. In the polymer obtained from triple-distilled diethylidichlorosilane the linear structure has already become pronounced. The increase in specific viscosity per elementary cell over the same period of time (24-48 hours) amounts, for once - distilled diethylidichlorosilane, to

\[
\begin{align*}
\text{poly (C}_2\text{H}_5\text{)}_n & \quad \frac{\Delta \eta_{sp}}{\Delta M} \quad \frac{\Delta \eta_{sp} \cdot M_{cell}}{\Delta M} \quad 0.43 \times 10^{-2}
\end{align*}
\]
where $\eta_{sp} = \eta - 1$; $M$ = molecular weight of a unit of the chain.

For triple-distilled diethyldichlorosilane, the value of $\Delta \eta_{sp}/(C_2H_5)_2SiO$ is about 10 times as high, and now amounts to $4.28 \times 10^{-2}$.

Table 65

Effect of the Purity of the Starting Diethylchlorosilane on the Properties of the Polymer

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c)</th>
<th>d)</th>
<th>e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>f)</td>
<td>0</td>
<td>815</td>
<td>0.021</td>
<td>—</td>
</tr>
<tr>
<td>24</td>
<td>1450</td>
<td>0.032</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>48</td>
<td>2040</td>
<td>0.057</td>
<td>9.8</td>
<td></td>
</tr>
<tr>
<td>72</td>
<td>4850</td>
<td>insoluble</td>
<td>16.1</td>
<td></td>
</tr>
<tr>
<td>g)</td>
<td>0</td>
<td>410</td>
<td>0.015</td>
<td>—</td>
</tr>
<tr>
<td>24</td>
<td>665</td>
<td>0.049</td>
<td>40.4</td>
<td></td>
</tr>
<tr>
<td>48</td>
<td>1120</td>
<td>0.240</td>
<td>50.7</td>
<td></td>
</tr>
<tr>
<td>72</td>
<td>2040</td>
<td>insoluble</td>
<td>54.7</td>
<td></td>
</tr>
</tbody>
</table>

a) Diethyldichlorosilane; b) Time of condensation at 200°C, hours; c) Molecular weight of polymer (Cryoscopic); d) Specific viscosity of a 2% solution of the polymer in toluene; e) Condensation losses, %; f) Once-distilled g) Triple distilled

The considerable amount of the losses of volatile substances on the condensation of the hydrolyzates of thrice-purified diethyldichlorosilane is connected with the fact that two reactions of equal probability take place during hydrolysis and condensation: formation of a linear polymer with hydroxyl end-groups, and of a cyclic polymer of low molecular weight and low boiling point, for which the possibility of further condensation has already been lost. In the case of diethyldichlorosilane containing an admixture of ethyldichlorosilane, the cyclic products formed contain trifunctional units, and, in this way, are able to participate in further condensation, with the formation of high-polymer nonvolatile products (Bibl.178).

I have studied (Bibl.187) the process of hydrolysis of diethyldichlorosilane...
by an excess of water (3 mols of water to 1 mol of diethyldichlorosilane) and of the polycondensation of the hydrolyzates (cf. Fig. 30). On condensation, the molecular weight of the polymer, determined by the viscosimetric method, sharply rises in the first two hours of heating. On further heating, the increase in molecular weight slows down, and after 10 hours the molecular weight remains practically constant thereafter. Prolonged heating of the resin converts it into the insoluble state. The resin obtained was separated into fractions by extraction with the corresponding solvents.

The molecular weight of the starting resin was 5387 (determined cryoscopically in benzene) and 5401 (determined viscosimetrically), which corresponds to about 52 elementary units in the molecule. The resins were successively extracted with ethanol and benzene. The fraction soluble in ethanol had an average molecular weight of 4331 (cryoscopic) and 4551 (viscosimetric). The fraction obtained after extraction with benzene had a molecular weight of 6278 (cryoscopic) and 6483 (viscosimetric). The close agreement between the molecular weights, determined viscosimetrically and cryoscopically, indicates the linear structure of the polymer and its relatively low polydispersion just as in the case of the polydimethylsiloxanes. The process of condensation of polydiethylsiloxanes is accelerated in the presence of the esters of boric acid, triethanolamine, sulfuric acid, benzoyl peroxide, and other compounds. The reaction between phosphoric anhydride and polydiethylsiloxane has been investigated in detail. The starting polymer was mixed with various amounts of phosphoric anhydride, after
which the mixture was heated at 200°C for 24 hours. On the completion of the heating, the phosphoric acid was washed off the polymer, and the molecular weight of the polymer was determined by the cryoscopic method. When \( \text{P}_2\text{O}_5 \) is introduced into the polymer, the liberation of a large amount of heat and the formation of a gel or solid product is observed. After the phosphoric acid is washed away, however, the properties of the final product differ little from those of the starting polymer. The data on the properties of the starting and final products are as follows:

| Molecular Weight of Polymer before Treatment | 1,100 |
| Molecular Weight of Polymer after Heating | 630   |
| Molecular Weight of Polymer after Heating with Various Amounts of \( \text{I}_2\text{O}_5 \) |
| 3 eq \( \text{P}_2\text{O}_5 \) | 580   |
| 10 eq \( \text{P}_2\text{O}_5 \) | 580   |
| 20 eq \( \text{P}_2\text{O}_5 \) | 150   |

When polydiethyilsiloxane reacts with phosphoric anhydride, two competing reactions take place:

\[
\text{Si}-\text{OH} + \text{H} + \text{Si} \rightarrow \text{Si} - \overset{\cdot}{\text{O}} - \text{Si} + \text{H}_2\text{O} \quad \text{(I)}
\]

\[
\text{Si} - \overset{\cdot}{\text{OH} + \text{P} - \overset{\cdot}{\text{O}} - \text{P} + \text{H}_2\text{O} + \text{Si} \rightarrow \text{Si} - \overset{\cdot}{\text{O}} - \overset{\cdot}{\text{P}} - \overset{\cdot}{\text{O}} - \overset{\cdot}{\text{P}} - \overset{\cdot}{\text{O}} - \text{Si} \quad \text{(II)}
\]

The first reaction is connected with the cleavage of water from the two hydroxyl groups attached to the silicon. The phosphoric anhydride, as a dehydrating agent, has an accelerating action on this process. The second reaction consists in the formation of an organophosphorosilicon compound as a result of the reaction of the \( -\text{Si-OH} \) group with \( \text{P}_2\text{O}_5 \). The \( -\text{Si-O-P} \) bond is weak, and, in contrast to the...
-Si-O-Si- bond, is readily hydrolyzed by water with the formation of the original organosilicon polymers and phosphoric acid.

It follows from the above data that the reaction between phosphoric anhydride and polydiethyldisiloxane, with an insignificant amount of P₂O₅, proceeds partly by scheme I. The fundamental direction of the reaction, however, which is particularly clearly expressed in the case of large amounts of P₂O₅, is the formation of a mixed organophosphorusilicon compound, which is easily hydrolyzed by water during the subsequent washing.

The higher dialkyldichlorosilanes are hydrolyzed according to the same schemes of reaction as diethyldichlorosilane. The rate of hydrolysis and condensation of the higher polydialkyldisiloxanes depends to a considerable extent on the nature of the organic radical attached to the silicon. Thus, for example, tert-dibutyl dichlorosilane is not hydrolyzed by water, and its chlorine content cannot be determined by titration with alkali. This can be explained by the fact that the branched organic radicals cause steric hindrance on the hydrolysis of tert-dibutyl dichlorosilane (Bibl.179).

The reaction of hydrolysis of phenyltrichlorosilane and of diphenyldichlorosilane has been investigated in detail (Bibl.180, 188). The hydrolysis of diphenyldichlorosilane and the condensation of the initial hydrolyzate, diphenylsilanediol, take place so slowly that all the intermediate products in the process of transition from diphenyldichlorosilane to the polydiphenyl disiloxanes have been isolated, and the mechanism of this process is one of the examples for the explanation of the mechanism of the reactions of hydrolysis and condensation of the dialkyldichlorosilanes. On hydrolysis of diphenyldichlorosilane in an alkaline medium, the sodium salts of diphenylsilanediol are formed, and diphenylsilanediol can be isolated from it by cautious acidification of the mixture with acid (Bibl.181).

Diphenylsilanediol is also obtained in good yield on the hydrolysis of
diphenyldichlorosilane in an acid medium in the presence of a solvent (Bibl.182).

**Hydrolysis of Diphenyldichlorosilane to Diphenylsilanediol.** To a mixture of 77 ml of toluene, 161 ml of tertiary amyl alcohol, and 666 ml of water, 260 g of diphenyldichlorosilane dissolved in 77 ml of toluene is added dropwise, cooling to 25°C. After 30 minutes, during which all the diphenyldichlorosilane is added, the mixture is stirred for another 10 minutes. The solution is then filtered off from the precipitated crystals of diphenylsilanol, which are washed with water to remove the free acid, and are dried in the air. The diphenylsilanediol so obtained is practically free from polymeric products. It may be further purified by recrystallization from a mixture of methylethyl ketone and chloroform. The yield of the pure product is 93% of theoretical, melting point 118°C.

When treated with acids or alkalies, diphenylsilanediol readily forms cyclic polymers. Hexaphenylcyclotrisiloxane is obtained when diphenylsilanediol is heated in the presence of acid.

**Preparation of Hexaphenylcyclotrisiloxane.** In 150 ml of ether, 10 g of diphenylsilanediol is dissolved, and 5 ml of concentrated HCl is added to the solution. The mixture is boiled under a reflux condenser for 3 hours, then the ether is distilled off, and the residue is recrystallized from glacial acetic acid or a mixture of benzene and ethanol.

**Preparation of Octaphenylcyclotetrasiloxane.** To a boiling solution of diphenylsilanediol in 95% ethanol, 1-2 drops of an aqueous alkali solution is added. On cooling the solution, the tetramer crystallizes out. For its complete purification it may be recrystallized from a mixture of benzene and ethanol, or from glacial acetic acid.

On prolonged heating of diphenylsilanediol above the melting point, it condenses to form cyclic and linear polymers.

In a distillation flask, in vacuo, 20 g of diphenylsilanediol is heated.
first water is liberated, and then, at a higher temperature, from 300 to 330°C (1 mm), 7.6 g of impure hexaphenylcyclotrisiloxane is distilled. The residue in the flask, 7.5 g, consists of higher molecular cyclic and linear polyphenylsiloxanes, built up of rings linked by the siloxane bond.

Polyphenylcyclosiloxanes are solid crystalline substances. Octaphenylcyclo-tetrasiloxane is known in two crystalline modifications. It crystallizes from hot acetone in long thin monoclinic needles, while from cold acetone, in difference, triclinic rectangular plates are precipitated (Bibl.183). The temperature of transition from the unstable triclinic form to the stable monoclinic form is about 100°C. On heating to this temperature, the crystals of unstable form become lusterless. Cyclic polydiphenylsiloxanes have the following properties:

<table>
<thead>
<tr>
<th></th>
<th>Melting Point, °C</th>
<th>Boiling Point, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexaphenylcyclotrisiloxane</td>
<td>190</td>
<td>290-300 (1 mm)</td>
</tr>
<tr>
<td>Octaphenylcyclotetrasiloxane</td>
<td>201-202</td>
<td>330-340 (1 mm)</td>
</tr>
</tbody>
</table>

On partial hydrolysis of diphenyldichlorosilane, linear dichloropolyphenylsiloxanes are formed. In this case the hydrolysis is conducted in a homogenous medium, in a solvent that dissolves both water and diphenyldichlorosilane.

4 mols of diphenyldichlorosilanes are dissolved in 1000 ml of ether. To this mixture a solution of 2 mols of water in 400 ml of dioxane is added dropwise with vigorous stirring. After addition of the water, dry nitrogen is blown through the mixture to remove the HCl, after which the solvent is distilled off and the residue is fractionated.

Dichlorohexaphenyltrisiloxane on fractionation is usually contaminated by hexaphenylcyclotrisiloxane, whose boiling point is close to its own. These two products are separated by extracting the dichlorohexaphenyltrisiloxane by n-heptane. The residue after fractionation probably contains higher molecular dichloropolydiphenylsiloxanes. When the molar ratio between water and diphenyldichlorosilane is
increased to 1 : 1.5, the yield of dichlorohexaphenyltrisiloxane is increased, while
the yield of dichlorohexaphenylbisiloxane is decreased. At a molar ratio of 1 : 1
or 1 : 0.67 between water and diphenyldichlorosilane, the reaction products consist
almost exclusively of hexaphenylcyclotrisiloxane (Bibl.189). The dichloropolydi-
phenylsiloxanes have the following properties.

<table>
<thead>
<tr>
<th></th>
<th>Melting Point, °C</th>
<th>Boiling Point, °C</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dichlorotetraphenyldisiloxane</td>
<td>38</td>
<td>238-241</td>
<td>Waxy Hexagonal Prisms</td>
</tr>
<tr>
<td></td>
<td>(1 mm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dichlorohexaphenyltrisiloxane</td>
<td>290-303</td>
<td></td>
<td>Waxy Amorphous Substance</td>
</tr>
<tr>
<td></td>
<td>(1 mm)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

On hydrolysis of dichloropolydiphenylsiloxanes by the method described for the
preparation of diphenylsilanediol, the corresponding linear polymers with hydroxyl
groups at the ends of the chains are formed. The hydrolysis of the dichloropolydi-
phenylsiloxanes proceeds considerably more slowly. To purify the dihydroxypolydi-
phenylsiloxanes, they are recrystallized from a mixture of benzene and n-heptane.
The yields of the products are 90-95% of theoretical.

The melting points of dihydroxypolydiphenylsiloxanes are as follows:

<table>
<thead>
<tr>
<th></th>
<th>Melting Point, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dihydroxytetraphenyldisiloxane</td>
<td>113-114</td>
</tr>
<tr>
<td>Dihydroxyhexaphenyltrisiloxane</td>
<td>111</td>
</tr>
</tbody>
</table>

On hydrolysis of diphenyldichlorosilane by a stream of moist air passed through
a solution of this substance in chlorobenzene, the formation of polymeric products
of cyclic and linear character is observed (Bibl.188).

The control of the process is effected by determining the acid value of the
reaction mass (Fig.31).

After 80 hour treatment of a solution of diphenyldichlorosilane at 50°C with a
stream of moist air, the acid number has been reduced to 11.6 mg KOH. This means
that the hydrolysis has been 97.8% completed. Similar experiments on the hydrolysis of a solution of diphenyldichlorosilane by moist air at 150°C have shown that the acid values of the reaction mass are gradually lowered. After 80 hours, the acid value of the reaction mass is 30.7 mg of KOH, which corresponds to a 94.2% level of hydrolysis.

The relative viscosity of the hydrolyzate gradually increases during the first 10-50 hours; thereafter it varies only slowly. The cause of the viscosity curve is evidence that the length of the polymer chain increases simultaneously with the process of hydrolysis (Fig. 32).

The polymer, after the solvent has been distilled off, is a dense nonuniform resinous mass containing inclusions of crystals which are probably hexapheny cyclo-trisiloxane. On further heating of the product at 150-200°C for 40 hours, the properties of the polymer change little. On heating, the product is gradually converted into a hard resin of melting point about 56°C.

The hydrolysis of organosilanes containing alkyl and aryl radicals attached to the same silicon atom by the action of water in an acid medium takes place with the
formation of viscous products from which cyclic and linear substances are isolated (Bibl.181). Phenylethylidichlorosilane on hydrolysis with water is converted into phenylethylsilanediol, which is then condensed to polyphenylethylsiloxane:

\[
C_6H_5(C_2H_5)SiCl_2 + 2H_2O \rightarrow C_6H_5(C_2H_5)Si(OH)_2 + 2HCl
\]

These two reactions are evidently consecutive, but they may also take place simultaneously.

Hydrolysis of Phenylethylidichlorosilane. To 600 ml of water, over a period of 3-4 hours, at a temperature below 70°C, 375 g of phenylethylidichlorosilane is drop-wise added with vigorous stirring. An oily product of moderate viscosity is obtained. When the water is introduced into the chloride, instead, a similar product is obtained. Hydrolysis by ammonia water, and also hydrolysis of a product that has first been esterified, yield the same result.

Studies have shown that the polyphenylethylsiloxanes formed on hydrolysis are cyclic compounds containing a trimer of the following structure:

\[
\begin{array}{c}
\text{Si--O--Si--C}_6\text{H}_5 \\
\text{Si--O--Si--C}_6\text{H}_5 \\
\end{array}
\]

On heating the hydrolyzate of phenylethylidichlorosilane by slowly blowing air at 190°C through it for 24 hours, the product becomes viscous and tacky. Acetaldehyde was found in the off-gases. The heating of the hydrolyzate to 180°C with simultaneous dropwise addition of aqueous HCl for 24 hours likewise leads to the formation of a viscous and tacky product. After 48 hours, most specimens are converted into an elastic gel insoluble in toluene, which contains 49.6% of silicon.
dioxide and has an average molecular weight of 1310, corresponding approximately to the following compounds:

\[
\begin{align*}
&\text{H}_2\text{C}_2\text{SiO}_2\text{SiH}_2 \\
&\text{H}_2\text{C}_2\text{SiO}_2\text{SiH}_2 \\
&\text{H}_2\text{C}_2\text{SiO}_2\text{SiH}_2 \\
&\text{H}_2\text{C}_2\text{SiO}_2\text{SiH}_2 \\
&\text{H}_2\text{C}_2\text{SiO}_2\text{SiH}_2
\end{align*}
\]

On treatment of the polymer with aqueous HCl, cleavage of the phenyl groups and liberation of benzene in an amount 67% of the theoretical takes place. The process proceeds by the scheme:

\[
2\text{SiC}_6\text{H}_{11} + \text{H}_2\text{O} \rightarrow 2\text{SiO} + 2\text{C}_6\text{H}_6
\]

The blowing of air through the liquid hydrolyzate of methylphenyldichlorosilane at 250°C leads to the formation of a soluble viscous tacky resin. In this case formaldehyde is liberated. The resin contains 6.4% of silica. In this case, if the product of hydrolysis of diphenylmethyldichlorosilane is treated with aqueous HCl at 170°C, the condensation product will contain 47.7% of SiO₂. The SiO₂ content of a coagulated specimen is 55.6%, which is evidence of the continuing cleavage of phenyl groups under the action of aqueous HCl at 170°C on the product.

Cyclic and linear polymethylphenylsiloxanes have been prepared and investigated. Their catalytic transformations under the actions of high temperature and catalysts have also been studied. For this purpose, methylphenyldichlorosilane is hydrolyzed by a mixture of water and ice, without solvent. The oil obtained by hydrolysis is heated in vacuo at 2 mm pressure to a temperature of 460°C. Under these conditions, a rearrangement of the siloxane bonds is possible. The fractional distillation of the oil so obtained yielded a cyclic trimer, which, as was established, consists of two stereoisomeric forms. The cis-isomer melts at 99.5°C, the trans-isomer at 39.5°C.
The cyclic polymethylphenylsiloxanes could be converted into linear products, as usual, by the action of sulfuric acid in the presence of hexamethyldisiloxane. It is well known, however, that the phenyl groups attached to the silicon atom are cleaved under the action of sulfuric acid, and this method is therefore inconvenient. It has been found that the cyclic polydimethylphenylsiloxanes may be converted into linear compounds under the action of a solution of caustic potash in a medium of isopropyl alcohol. In this case tetramethyldiphenylsiloxane may be used to induce ring closure. If hexamethyldisiloxane is used for this purpose, however, toluene must be added as a solvent, since hexamethyldisiloxane is miscible only within certain limits with isopropyl alcohol and with the polydimethylphenylsiloxanes. On the reaction between sym-tetramethyldiphenyldisiloxane and polymethylphenylsiloxanes in the presence of alkali, methylphenylsilanol and dimethylphenylisopropoxysilane are obtained. It may be postulated that the following equilibrium is established in this reaction:

\[
\text{KOH} \quad \text{ROH} \quad \overset{\text{H}_2\text{O}}{\longrightarrow} \quad \text{ROH} \quad \overset{\text{KOH}}{\longrightarrow} \quad \text{ROH}
\]

**Conversion of Cyclic Polymethylphenylsiloxane into the Linear Polymer.** Tetramethyldiphenyldisiloxane, 24.5 g or 0.057 mol, is mixed with 75 ml of isopropyl alcohol and 38.8 g or 0.275 mol of cyclic dimethylphenylsiloxanes. To the homogeneous solution so obtained, 8 ml of a 60% solution of KOH in water is added. Only 5.3 ml of the alkali solution dissolves. The mixture is then heated 39 hours at 71°C. After cooling, the mixture is first washed with a 10% solution of sodium chloride to break the emulsion, then with a 10% solution of ammonium chloride, and the organic layer is then dried. The propyl alcohol is distilled off and the residue is fractionated, yielding the following fractions: 60-119°C (1.8 mm), 15.1 g; 120-138°C (2 mm), 166.5 g (tetramethyldiphenyldisiloxane found); 130-173°C (0.5 mm), 59.3 g (mainly the linear trimer found); 25.3 g of residue with a lower viscosity than the...
starting polymethylphenylsiloxanes. This residue probably consists of products of linear structure.

The low boiling fraction is redistilled, yielding 2.8 g of a product of boiling point 65-66°C (3.5 mm). Its analysis confirmed the fact that this fraction consists of dimethylphenylsilanol. The presence of dimethylphenylpropoxysilane in this same fraction was qualitatively established.

Study of the Structure of Cyclic Polysiloxanes

As already stated, cyclic products are often the principal reaction products of the hydrolysis of dialkyldichlorosilanes, especially in acid media, and a study of their structure is therefore of considerable interest. The cyclic trimers and tetramers are most often formed. If the size of the organic radical is small, the trimer and tetramer can be separated by fractional distillation in vacuo. It is also necessary, however, to determine the molecular weight of the product, its structure, and a number of other characteristics. The use of the method of infrared spectroscopy to establish the nature of cyclic polysiloxanes gives good results. A number of cyclic polymers have been prepared to investigate the infrared spectra (Bibl.176).

Preparation of Hexaethylcyclotrisiloxane and Octaethylcyclotetrasiloxane. To a solution of 478 g of diethyldichlorosilane in 700 ml of ether, 478 g of ice is added. After all the ice has melted, the mixture is boiled 1 hour under a reflux condenser. The water layer is separated, and the ether layer is washed once with an equal volume of water. The washed ether solution is boiled with a 5% solution of caustic soda with the object of completing the hydrolysis of the unreacted chlorine atoms and also of effecting more complete condensation. After distilling off the ether, a transparent colorless liquid containing 62% of volatile cyclic polymers is obtained. The hydrolysis of diethyldichlorosilane with ice, without using a solvent, formed a product containing 27% of volatile cyclic polymers. Hydrolysis of diethyldichloro-
silane by adding it dropwise to boiling water gives a product containing only 22% of volatile cyclic polymers.

Fractional distillation of the hydrolyzate yields 60-70% of a cyclic trimer with the following properties:

- **Melting Point °C**: 9.9
- **Boiling Point °C**: 156.7 (50 mm)
- **Specific Gravity**: 0.9549
- **Refractive Index**: 1.4308
- **Viscosity at 25°C, Centistokes**: 3.6

and 10-20% of a cyclic tetramer with the following properties:

- **Freezing Point °C**: -64°C
- **Boiling Point °C**: 127°C (1 mm)
- **Specific Gravity**: 0.964
- **Refractive Index**: 1.4336
- **Viscosity at 25°C, Centistokes**: 11.2

**Preparation of 1,2,3-Trimethyltriphenylcyclotrisiloxane and 1,2,3,4-Tetramethyltetraphenylocyclotetrasiloxane.** Pure methylphenyldichlorosilane, 500 g, is diluted with 3 parts by volume of ether, and a mixture is cooled by placing the flask in an ice bath. To the cooled mixture, 370 ml of water per mol of methylphenyldichlorosilane is added. The ether solution is then washed with distilled water until free of chlorine. After distilling off the ether in vacuo at 20 mm, up to 100°C, the residue is a colorless oil with the following properties:

- **Specific Gravity**: 1.125
- **Viscosity at 20°C, Centistokes**: 203
- **Refractive Index**: 1.5451
Vacuum distillation of the product from a short-necked flask up to a temperature of 300°C, at 0.1 mm, yields 76.7% of volatile products of the following properties:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Gravity</td>
<td>1.121</td>
</tr>
<tr>
<td>Viscosity at 20°C, Centistokes</td>
<td>187</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>1.5445</td>
</tr>
</tbody>
</table>

When the fraction boiling at 157°C (0.1 mm) is collected while crystals begin to be thrown down in the receiver. They are filtered off from the mother liquor, and are recrystallized from methanol. The crystals have a melting point of 100°C.

A study of the infrared spectra of this product has shown it to be phenylmethylcyclotrisiloxane. When the mother liquor stands for a few days, at room temperature, no further crystallization of the product is observed. On standing in a refrigerator at -20°C, however, all the liquid becomes very much denser, and then crystallizes out completely at room temperatures. The crystals so obtained, after recrystallization from methanol, have a melting of 45.5°C.

The infrared spectrum of this compound indicates that it is also a cyclic trimer, but in the spectra of both products insignificant but entirely distinct differences are perceptible, which can be explained by the fact that they are stereoisomers. The fraction corresponding to the cyclic tetramer is collected in such a way that when the area corresponding to the tetramer appears on the rectification curve, the fraction is collected not in one receiver, but in several, and the fraction is separated into several parts.

After the several parts of this fraction are allowed to stand for a few weeks, in these receivers, about 15-20% of white crystals are thrown down, which are recrystallized from methanol. After recrystallization they have the melting point of 99°C.

A study of the infrared spectrum of this product has shown that the crystals,
like the mother liquor, consists of tetramer. The spectra of these substances some-
what differ from each other. When the liquid tetramer has stood for three weeks,
no crystalline products whatever are found to separate.

Preparation of 1,2,3-Triethylphenylcyclosiloxane and 1,2,3,4-Tetraethyl-
tetraphenylcyclotetrasiloxane. To 770 g of ground ice 510 g of ethylphenylidichloro-
silane dissolved in 3 volumes of ether is gradually added. After the ice has melted
the mixture is boiled an hour under a reflux condenser. The ether layer is then
washed with water, and an equal volume of a 5% solution of caustic soda is added.
The mixture is again boiled for some time under a reflux condenser.

The water-alkaline layer is separated, and the ether layer is washed at first
in a 2% HCl solution, then with distilled water until the reaction is neutral, and
is then dried over calcium chloride. The ether is distilled off during heating of
the solution to 150°C (50 mm). The colorless oil so obtained is placed in a short-
necked flask. The contents of the flask are heated to 280°C (0.05-0.1 mm), and
77.5% of volatile products are then distilled off.

At a temperature of 25°C, the distillate has a viscosity of 21 centistokes.

The distillate, amounting to 530 g (from 3 experiments) is fractionated in a
column, yielding 260 ml of a fraction boiling at 170-175°C (0.1 mm), and 120 ml of
a fraction boiling at 212°C (0.1 mm). Redistillation of each in the same column
yields 230 ml of a fraction consisting of cyclic trimer boiling at 166°C (0.025 mm).
The refractive index is 1.5102, the specific gravity 1.0932, the viscosity at 25°C,
63.6 centistokes.

After the product was allowed to stand for 4 hours, no crystal had separated
out. On considering the spectrum of this compound it may be concluded that it is
pure 1,3,5-triethyltriphenylcyclosiloxane, free from the cyclic tetramer.

The fraction boiling at 212°C (0.1 mm) has a viscosity of 25°C of 220 centi-
stokes, a refractive index of 1.5130, and a specific gravity of 1.1000. After stand-
ing for three weeks at room temperature, white crystals begin to separate out from
this fraction. They are filtered off and recrystallized twice from absolute methanol. The melting point of the crystal is 106°C, and the yield is 10-11 g, that is, about 10%.

A study of the infrared spectrum of this compound leads to the conclusion that it is the pure cyclic tetramer. The mother liquor is also pure tetramer.

Tetraethyl-1,2-diphenylcyclotrisiloxane is obtained by cohydrolysis of a mixture of 2 mols of diethyldichlorosilane and 1 mol of ethylphenyldichlorosilane by the method described above. A complex mixture of cyclic products is formed, which on fractionation yields about 15% of tetraethyl-1,2-diphenylcyclotrisiloxane; boiling point, 150°C (0.5 mm); refractive index, 1.5008; specific gravity, 1.0561.

On rectification, 240 ml of a substance passing over at 165°C (12 mm) is collected. This fraction consists mainly of pentaethylphenylcyclotrisiloxane. Refractive index 1.4735; specific gravity 1.0096.

A study was made of the infrared spectra of solutions prepared by dissolving 500 mg of product in 5 ml of CCl₄, for wavelengths from 2 to 7.5 μ, and 100 mg of product in 5 ml of C₂H₆, for wavelengths from 7.5 to 16 μ. Since hexaphenyldicyclo-
trisiloxane is sparingly soluble in CCl₄, it was studied in the form of a considerably more dilute solution - 5%. The study was made in a cell 0.2 mm thick.

For the methyl group attached to the silicon atom, the following absorption bands are characteristic: 3.38, 7.08 and 7.91 μ. For the ethyl groups, bands were noted at 6.84, 7.08, 7.26, 8.05, 9.9 and 10.4 μ. The phenyl group has bands at 6.28, 6.7, 6.98, 8.4, 8.9, 9.7, and 10.04 μ. Each of these bands has a width of a few hundredths of a micron and shows slight fluctuations of intensity for a different compound.

Three bands characteristic for the methyl groups correspond to stretch vibrations of the C-H bond, to the bending vibrations of this bond, and to the vibrations of the methyl group, respectively. Another sharp band between 12 and 13μ is characteristic for the stretch vibrations of the Si-C bond.
Phenomena of stereoisomerism are also observed in the cyclic polysiloxanes. Thus, for instance, for the four-membered rings, in which each atom of silicon is attached to two different radicals, the following four structures are possible:
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CHAPTER VII

HYDROXYL-DERIVATIVE ORGANOSILANES

The hydroxyl-derivative silanes are the fundamental monomeric compounds whose polycondensation leads to the formation of polysiloxanes. Theoretically the following hydroxyl derivatives of silane may exist:

\[ H_2SiOH \rightarrow H_2Si(OH)\_2 \rightarrow HSi(OH)\_n \rightarrow Si(OH)\_n \]

Owing to their exceptional tendency to condensation, the hydroxyl derivatives of silane, except for dihydroxysilane \( H_2Si(OH)\_2 \), have not been isolated in the monomeric form. 0.5 cm\(^3\) of dihydroxysilane has been prepared, but its properties could not be studied, since condensation of the product soon occurred (Bibl.1). The molecular weight of its condensation products is 296 (which corresponds to the hexamer).

The hydroxysilanes may possibly be formed as intermediates in many reactions.

On the hydrolysis of a monohalosilane, the formation of monohydroxysilane is postulated (Bibl.1).

\[ H_2SiCl + H_2O \rightarrow H_2SiOH + HCl \]

Monohydroxysilane condenses immediately to form disiloxane.

Hydrolysis of a dihalosilane leads to the formation of dihydroxysilane, which rapidly condenses to form polymers.

It is postulated that on the hydrolysis of a trihalosilane, trihydroxysilane is
formed and then immediately condenses.

The organodihydroxysilanes are of greater practical interest:

\[ R_3Si(\text{OH})_2, R_2Si(\text{OH})_3 \text{and } RSi(\text{OH})_3 \]

**Organomonohydroxysilanes**

On condensation of organohydroxysilanes of the type \( R_3Si\text{OH} \), only the dimers, organodisiloxanes \( R_3SiOSiR_3 \), can be formed. On co-condensation with organodihydroxysilanes and organotrihydroxysilanes, however, they participate in the construction of chains of polyorganosiloxanes of higher molecular weight, and, by adding their single hydroxyl group to the polyorganosiloxane chain, they block its growth. Thus, the organohydroxysilanes are of interest in cases where inert polymeric compounds with short chains must be prepared.

The most widely used and generally recognized reactions forming organohydroxysilanes are the reactions of hydrolysis of trialkyl- and triarylchlorosilanes, of tri-substituted esters of orthosilicic acid, and of certain other compounds.

The first representative of this class of compounds, trimethylhydroxysilane, is formed directly on the hydrolysis of trimethylchlorosilane in an alkaline medium:

\[
\begin{align*}
(\text{CH}_3)_3\text{SiCl} + \text{NaOH} & \rightarrow (\text{CH}_3)_3\text{SiONa} + \text{HCl} \\
(\text{CH}_3)_3\text{SiONa} + \text{H}_2\text{O} & \rightarrow (\text{CH}_3)_3\text{SiOH} + \text{NaOH}
\end{align*}
\]

Monomeric trimethylhydroxysilane is formed in small quantities on the hydrolysis of trimethylchlorosilane by a 1 N solution of an alkali in an ethereal solution. The principal product of this reaction is hexamethyldisiloxane which, together with trimethylhydroxysilane, forms an azeotropic mixture, so that trimethylhydroxysilane can be separated only with difficulty in the pure state. On hydrolysis of trimethylfluorosilane by a weak solution of alkali, in ethereal solution, and at low temperature, trimethylhydroxysilane is formed. The yield is 70% of theoretical.

**Preparation of Trimethylhydroxysilane (Bibl.2).** An ethereal solution of trimethylfluorosilane (cf.p.457) is titrated, under strong cooling, with an NaOH solu-
tion to a neutral reaction with phenolphthalein. The ethereal layer is separated from the water, the aqueous layer is twice extracted with ether in 100 ml portions, and the ethereal extracts are combined and fractionated. Trimethylhydroxysilane boils at 99°C (734 mm).

Hydrolysis of trimethylbromosilane under similar conditions leads to the formation of hexamethyldisiloxane.

When methylmagnesium bromide acts on polymeric polydimethylsiloxane, followed by hydrolysis of the reaction products, trimethylhydroxysilane is formed (Bibl.3):

\[
\left[(\text{CH}_3)_{x}\text{SiO}\right]_x + x\text{CH}_3\text{MgBr} \rightarrow x(\text{CH}_3)_x\text{SiOMgBr}
\]

\[
(\text{CH}_3)_x\text{SiOMgBr} + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_x\text{SiOH} + \text{MgBrOH}
\]

Trimethylchlorosilane reacts with liquid ammonia to form hexamethyldisiloxane, a liquid boiling at 126°C (758 mm).

\[
2(\text{CH}_3)_x\text{SiCl} + \text{NH}_3 \rightarrow (\text{CH}_3)_x\text{SiNHSi}(\text{CH}_3)_x + 2\text{HCl}
\]

On hydrolysis of hexamethyldisiloxane by water or aqueous alkali, trimethylhydroxysilane is formed:

\[
(\text{CH}_3)_x\text{SiNHSi}(\text{CH}_3)_x + 2\text{H}_2\text{O} \rightarrow 2(\text{CH}_3)_x\text{SiOH} + \text{NH}_3
\]

On the acid hydrolysis of hexamethyldisiloxane, only hexamethyldisiloxane is formed.

Hydrolysis of trimethylchlorosilane by an excess of water leads to the formation only of hexamethyldisiloxane (boiling point 100°C). Hydrolysis of an ethereal solution of trimethylchlorosilane by a 20% aqueous KOH solution leads to an azeotropic mixture of hexamethyldisiloxane and trimethylhydroxysilane.

Trimethylhydroxysilane is obtained when a mixture of polymeric dimethylsiloxane and methylmagnesium iodide in a dibutyl ether medium is heated 2 hours on a water bath, followed by hydrolysis. It has the odor of camphor. It is dehydrated on boil-
ing (under a reflux condenser), and also by heating with dehydrating agents.

Dimethyldichloromethylhydroxysilane \((\text{CH}_3)_2(\text{CHCl}_2)\text{SiOH}\) is formed in slight quantities on the hydrolysis of dimethyldichloromethylchlorosilane in ethereal solution by ice water. Dimethyldichloromethylhydroxysilane is a liquid with the boiling point 89°C (40 mm).

Triethylhydroxysilane is obtained on hydrolysis of triethylchlorosilane.

Triethylhydroxysilane may be prepared by alkaline hydrolysis of triethyilsilane-sulfate:

\[
(\text{C}_3\text{H}_8)_2\text{SiOSO}_3\text{OH} + \text{H}_2\text{O} \rightarrow (\text{C}_3\text{H}_8)_2\text{SiOH} + \text{H}_2\text{SO}_4
\]

Triethylsilane sulfate is obtained by the action of 20% oleum on hexaethylidisiloxane, according to the reaction:

\[
(\text{C}_3\text{H}_8)_2\text{SiOSi}(\text{C}_3\text{H}_8)_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2(\text{C}_3\text{H}_8)_2\text{SiOSO}_3\text{OH} + \text{H}_2\text{O}
\]

Preparation of Triethylhydroxysilane. To 600 ml of dry ether, 151 g of triethylchlorosilane is added, and the solution is cooled on an ice bath. The solution, being vigorously agitated, is then slowly (30 min) titrated at 0°C with 1 N NaOH solution to neutral in the presence of phenolphthalein. The ether layer is removed, and the water layer is twice extracted with 100 ml portions of ether. The combined ethereal extracts are dried with calcined potassium carbonate and are then fractionated. Result 125 g of triethylhydroxysilane, boiling point 77.5°C (28 mm). The yield is 95%.

Preparation of Triethylsilane Sulfate (Bibl.). A mixture of 99 g of hexaethyl-disiloxane and 56 g of oleum is stirred for 30 min at room temperature. Then 10 g of ammonium sulfate is added to the reaction mixture, and it is again stirred for 2 hours at room temperature. The triethylsilane sulfate formed is extracted from the reaction mass with pentane. The pentane is evaporated off, and the residue is fractionated under reduced pressure. Triethylsilane sulfate has a boiling point of 170°C (12 mm). It decomposes partially on distillation.
α-Chloroethyldiethylhydroxysilane is formed on hydrolysis of α-chloroethyldiethylchlorosilane by alkali (Bibl.5):

\[(\text{CH}_3\text{CHCl})\text{Si}((\text{C}_2\text{H}_5)_2\text{Cl} + \text{NaOH} \rightarrow \text{NaCl} + (\text{CH}_3\text{CHCl})\text{Si}((\text{C}_2\text{H}_5)_2\text{OH})\]

**Preparation of α-Chloroethyldiethylhydroxysilane.** A mixture of 60 g of α-chloroethyldiethylchlorosilane, 200 g of ice, and 20 g of NaOH, is stirred for 30 min. The mixture heats up during the stirring, and toward the end of the process it must be cooled by a water bath with ice. The reaction product is extracted three times with ether in portions of 150 ml. The ethereal extracts are washed with water, dried with anhydrous magnesium sulfate, and fractionated. The α-chloroethyldiethylhydroxysilane distils at 101°C (29 mm). The yield of the product is 34% of theoretical.

In this reaction the formation of disiloxane is not observed, which speaks for the considerable stability of α-chloroethyldiethylhydroxysilane. Heating of the product with aqueous solutions of an alkali causes cleavage of the chloroethyl group:

\[(\text{CH}_3\text{CHCl})\text{Si}((\text{C}_2\text{H}_5)_2\text{Cl} + 2\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_5\text{Cl} + (\text{C}_6\text{H}_5)_2\text{Si(OH)}_2\]

The diethyldihydroxysilane that is formed is condensed, yielding polymeric products.

α-phenylhydroxysilane has also been prepared from triphenylbromosilane on hydrolysis with water in an alkaline medium by the method described above:

\[(\text{C}_6\text{H}_5)_2\text{SiBr} + \text{KOH} \rightarrow (\text{C}_6\text{H}_5)_2\text{Si(OH)} + \text{KBr}\]

Various hydroxysilanes have been prepared by the action of strong sulfuric acid on tetra-substituted silanes containing a single phenol group. Cleavage of the phenyl group takes place, giving the corresponding hydroxysilane (Bibl.6):
The reaction shown is:

\[
\text{CH}_3\text{SiC}_6\text{H}_5 + \text{H}_2\text{SO}_4 \rightarrow \text{CH}_3\text{SiC}_6\text{H}_5 + \text{C}_6\text{H}_5\text{SO}_4\text{H}
\]

The action of fuming HCl at 180°C has been found to be similar, from the example of the formation of triethylhydroxysilane from triethylphenylsilane.

The organodisiloxanes are hydrolyzed on heating with alkali, and are converted into hydroxysilanes (Bibl.7, 8):

\[
\text{(CsH}_8\text{)}_2\text{SiOSi}((\text{CsH}_8)_3 + \text{H}_2\text{O} \rightarrow 2(\text{CsH}_8)_2\text{SiOH}
\]

A large number of mixed hydroxysilanes can be prepared by hydrolysis of mixed chlorosilanes or mixed tri-substituted esters of orthosilicic acid in an alkaline medium:

\[
(\text{C}_2\text{H}_5)\text{(CsH}_8\text{)}(\text{CsH}_8)\text{SiCl} + \text{H}_2\text{O} \rightarrow (\text{CsH}_8)\text{(CsH}_8\text{)}(\text{CsH}_8)\text{SiOH} + \text{HCl}
\]

\[
(\text{C}_2\text{H}_5)\text{(CsH}_8\text{)}(\text{CsH}_8)\text{Si(OCH)}_{2} + \text{H}_2\text{O} \rightarrow (\text{CsH}_8)\text{(CsH}_8\text{)}(\text{CsH}_8)\text{SiOH} + \text{C}_2\text{H}_4\text{OH}
\]

**Physical Properties**

Trimethylhydroxysilane is a colorless liquid with a strong odor of camphor and a neutral reaction. It is dehydrated by prolonged distillation under atmospheric pressure; but when rapidly distilled a rather pure product is obtained. Prolonged storage at room temperature leads to some decomposition. Trimethylhydroxysilane is dehydrated at room temperature by most drying agents. The action of activated aluminum oxide and potassium carbonate on trimethylhydroxysilane at room temperature leads to the formation of insignificant quantities of hexamethyldisiloxane. The other trialkyldihydroxysilanes are colorless liquids with a pleasant odor. Only trimethyl- and triethylhydroxysilanes are partially soluble in water. All the trialkylhydroxysilanes are readily soluble in many organic solvents - alcohols, benzene, toluene, chlorinated hydrocarbons, and ethers. Distillation, either under reduced pressure or under atmospheric pressure, results in their condensation.
Table 66
Physical Properties of Trialkyl- and Triarylhdroxysilanes

<table>
<thead>
<tr>
<th>a) Name</th>
<th>b) Formula</th>
<th>c) Melting point</th>
<th>d) Boiling point</th>
<th>e) Specific gravity</th>
<th>f) Bibliography</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trimethylhydroxysilane</td>
<td>(CH₃)₃SiOH</td>
<td>—</td>
<td>100-97 (760 mm)</td>
<td>0.8112</td>
<td>3.37</td>
</tr>
<tr>
<td>Dimethyl dichloro-</td>
<td>(CH₃)₂CHCl₂SiOH</td>
<td>89</td>
<td>—</td>
<td>—</td>
<td>22</td>
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<tr>
<td>Triethylhydroxysilane</td>
<td>(CH₃)₃SiOH</td>
<td>153-154</td>
<td>—</td>
<td>0.8647</td>
<td>6.7</td>
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<tr>
<td>α-Chloroethyl diethyl-</td>
<td>(CH₂CHCl)₂SiOH</td>
<td>—</td>
<td>150</td>
<td>—</td>
<td>19</td>
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<td></td>
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<tr>
<td>Tripropylhydroxysilane</td>
<td>(C₃H₇)₃SiOH</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>23.24</td>
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<td>Triisopropylhydroxy-</td>
<td>(C₃H₇)₂CHSiOH</td>
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<td>207</td>
<td>—</td>
<td>37</td>
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<td></td>
</tr>
<tr>
<td>Tributylhydroxysilane</td>
<td>(C₄H₉)₃SiOH</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>26</td>
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<tr>
<td>Triisoamylhydroxy-</td>
<td>[(C₄H₉)CH₂CH₂CH₃Si(OH)]</td>
<td>—</td>
<td>270</td>
<td>—</td>
<td>11.37</td>
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<td>Triphenylhydroxy-</td>
<td>(C₆H₅)₃SiOH</td>
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<td>—</td>
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<td>25.25</td>
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<tr>
<td>Tri-p-tolylhydroxy-</td>
<td>[(C₆H₅)CH₃CH₂SiOH]</td>
<td>—</td>
<td>100</td>
<td>—</td>
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<td>Tribenzylhydroxysilane</td>
<td>[(C₆H₅)CH₂SiOH]</td>
<td>104-106</td>
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<td>26</td>
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<td>Methylethpropyl-</td>
<td>(CH₃)(C₆H₅)(C₆H₅)SiOH</td>
<td>—</td>
<td>165-185 (45 mm)</td>
<td>—</td>
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<td>Methylethphenyl-</td>
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<td>—</td>
<td>115</td>
<td>—</td>
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<td>Diethphenylhydroxysilane</td>
<td>(C₆H₅)(C₆H₅)SiOH</td>
<td>—</td>
<td>185</td>
<td>—</td>
<td>29</td>
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<td>Methylidibenzylhydroxy-</td>
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<td>—</td>
<td>241</td>
<td>—</td>
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<td>Ethypropylphenyl-</td>
<td>[(C₆H₅)CH₂(CH₃)]SiOH</td>
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<td>—</td>
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<td>Ethypropylbenzyl-</td>
<td>[(C₆H₅)CH₂CH₃SiOH]</td>
<td>—</td>
<td>250</td>
<td>—</td>
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<td>Ethyldibenzyl-</td>
<td>(C₆H₅)(C₆H₅)SiOH</td>
<td>—</td>
<td>155</td>
<td>—</td>
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<tr>
<td>Phenyldicyclohexyl-</td>
<td>(C₆H₅)(C₆H₅)SiOH</td>
<td>—</td>
<td>165</td>
<td>—</td>
<td>38</td>
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<tr>
<td>Ethylisobutylbenzyl-</td>
<td>[(C₆H₅)CH₂CH₃]SiOH</td>
<td>—</td>
<td>165 (40 mm)</td>
<td>—</td>
<td>30.37</td>
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<tr>
<td>Ethylbenzylhydroxy-</td>
<td>(C₆H₅)(C₆H₅)SiOH</td>
<td>—</td>
<td>165</td>
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<td>28.29</td>
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<td>165 (45 mm)</td>
<td>—</td>
<td>38</td>
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</tbody>
</table>

a) Name; b) Formula; c) Melting point; d) Boiling point; e) Specific gravity;
f) Bibliography
The triaryltidroxyxilanes are crystalline solids, soluble in many solvents but insoluble in alcohols and ligroin. Table 66 gives certain properties of the hydroxy- silanes.

The monohydroxysilanes recall organic alcohols. Their dipole moments are somewhat lower than in the alcohols (1.65 D), but higher than in the phenols (1.40 D). The dipole moment of triethylhydroxysilane is 1.50 D.

Chemical Properties

The chemical properties of the tertiary alcohols and those of the hydroxysilanes are different. The trialkyl- and triaryltidroxyxilanes, in contrast to the alcohols, have a tendency to condensation. With increasing size of the organic radical, the condensation of trialkylhydroxysilanes into hexaalkyldisiloxanes becomes somewhat more difficult. At the same time the reverse process of the breaking of the siloxane bond, giving trialkylhalosilanes, is facilitated. The reaction

$$\text{R}_3\text{SiOSiR}_3 + \text{H}_2\text{O} \rightarrow \text{R}_2\text{SiOH} + \text{R}_2\text{SiOH}$$

for hexamethyldisiloxane is markedly shifted toward the left. When triethylhydroxysilane is treated with concentrated HCl, however, its condensation into hexamethyl disiloxane is not observed. The reaction in this case is shifted toward the right, and the triethylhydroxysilane may be converted into triethylchlorosilane. The yield is 75% of theoretical. Under the action of HBr, triethylhydroxysilane is quantitatively converted into hexamethyldisiloxane; and no triethylbromosilane is formed in this case.

In spite of the relative ease of condensation of trialkylhydroxysilanes at the instant of their formation, especially in acid hydrolysis, the trialkylhydroxysilanes, once isolated, are rather stable. When triethylhydroxysilane is boiled with water, 0.01N HCl, or 0.01N alkali, only 10% of it is dehydrated, while 50% of tri-
methylhydroxysilane is dehydrated under the same conditions. Passage of triethylhydroxysilane over active aluminum oxide at 360°C results in only 8% dehydration.

The hydrogen in the hydroxyl group of trialkylhydroxysilanes is capable of reacting with metallic sodium, forming the trialkylsodium-oxysilane: the sodium derivative of trimethylsilanol (Bibl.9, 10):

\[ 2(\text{CH}_3)_3\text{SiOH} + 2\text{Na} \rightarrow 2(\text{CH}_3)_3\text{SiONa} + \text{H}_2 \]

When a trialkylhydroxysilane reacts with sodium in a solution of dry xylene, hydrogen is liberated quantitatively, and this reaction may be used for analytical purposes.

On the action of concentrated alkali (12 N) on trimethylsilanol, the sodium derivative of trimethylsilanol is formed, and is thrown down as a white precipitate. The reaction is conducted with vigorous stirring and cooling. When an aqueous suspension of the sodium derivative of trimethylsilanol is shaken with ether, the precipitate passes over into the ether layer, and in this way is separated from the water layer. The precipitate is washed with ether, and dried over phosphorus pentoxide. The yield of the product is 87% of theoretical.

The sodium derivative of trimethylsilanol can be recrystallized, with difficulty, from an ether-acetone mixture. It melts at 147 - 150°C, with partial decomposition. On the acid hydrolysis of the sodium derivative of trimethylsilanol, hexamethyldisiloxane is formed.

The literature also contains indications that when trimethylhydroxysilane reacts with lead oxide, hexamethylplumboxydisilane is formed:

\[ 2(\text{CH}_3)_3\text{Si(OH)} + \text{PbO} \rightarrow [(\text{CH}_3)_3\text{SiO}]_2\text{Pb} + \text{H}_2\text{O} \]

At an elevated temperature and pressure, hexamethyldisiloxane reacts with an aqueous solution of alkali to form methane and sodium silicate.

In 500 ml of 3N NaOH solution, 0.5 mol of hexamethyldisiloxane is dissolved,
and the solution is heated in an autoclave at 200°C. The yield of methane is 76% of theoretical.

Under the action of sulfuric acid on trimethylchlorosilane, hexamethylnifondioxysilane is formed.

**Preparation of Hexamethylnifondioxysilane.** To 23.8 g of trimethylchlorosilane 9.8 g of sulfuric acid is added dropwise, with vigorous shaking. HCl is evolved during the addition of the sulfuric acid, and in consequence the mixture is cooled of itself.

After all the sulfuric acid has been added, the reaction mixture is fractionated. The 87 - 90°C (4 mm) fraction is hexamethylnifondioxysilane, a white crystalline substance of the m.p. 45 - 46°C. When this substance is fractionated at higher pressures and temperatures, energetic decomposition and oxidation of the product was observed.

Triethylhydroxysilane reacts with 38%-HCl to form triethylchlorosilane. Under the action of strong HBr under the same conditions, only hexasthlydisiloxane is obtained.

Conversion of triethylhydroxysilane into triethylchlorosilane. Into a flask provided with a stirrer, 450 ml of concentrated HCl is poured. Under strong cooling with ice and stirring, 66 g of triethylhydroxysilane is added to the acid. The mixture is stirred 1 hour. The upper layer is then taken off, thoroughly dried with anhydrous zinc chloride, and fractionated in a column, yielding 58 g of triethylchlorosilane; boiling point 145°C (729 mm). The yield is 77% of theoretical.

Heating of triethylhydroxysilane with acetic anhydride produces triethylacetoxysilane.

For this purpose 26.4 g of triethylhydroxysilane is mixed with 20.4 g of acetic anhydride, and the mixture is heated 12 hours on the water bath at 100°C. Fractional distillation yields 26.2 g of triethylacetoxysilane; boiling point 167°C (726 mm). The yield is 76% of theoretical.
When triethylhydroxysilane is boiled 6 hours, dehydration does not occur. The sodium derivative of triisoamylsilanol \( [(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2]_3\text{SiONa} \) has been obtained by reacting triisoamylsilanol with sodium (Bibl.11).

When acetyl chloride acts on triethylhydroxysilane, \((\text{C}_2\text{H}_5)_3\text{SiOCH}_3\) triethylacetoxysilane is formed (Bibl.12).

Numerous studies of the action of acetyl chloride on triphenylhydroxysilane have shown that this reaction proceeds with chlorination of that compound:

\[
(\text{C}_6\text{H}_5)_3\text{Si(OH)} + \text{CH}_2\text{COCI} \rightarrow (\text{C}_6\text{H}_5)_3\text{SiCl} + \text{CH}_2\text{COOH}
\]

On heating in an acid medium, the hydroxysilanes condense readily to form dimers.

In comparing the properties of triphenylcarbinol and triphenylsilanol, Ipatiyev and Jolgov hydrogenated them. They found that triphenylcarbinol is completely hydrogenated to tricyclohexylmethane; triphenylsilanol is not hydrogenated under the same conditions, but is completely converted to hexaphenyldisiloxane:

\[
2(\text{C}_6\text{H}_5)_3\text{Si(OH)} \rightarrow (\text{C}_6\text{H}_5)_3\text{Si}--\text{O}--\text{Si}(\text{C}_6\text{H}_5)_3 + \text{H}_2\text{O}
\]

Experiments on the reduction of triphenylsilanol to triphenylmonosilane performed by the same authors showed that the reduction takes place only when zinc dust and acetic acid are used. A small amount of an oily substance resembling triphenylsilane was obtained.

An attempt to prepare phenylurethane by heating triphenylsilanol with phenyl isocyanate did not succeed. The reaction formed hexaphenyldisiloxane, carbon dioxide, and sym-diphenylurea instead:

\[
2(\text{C}_6\text{H}_5)_3\text{SiOH} \rightarrow 2\text{C}_6\text{H}_5\text{CNO} \rightarrow (\text{C}_6\text{H}_5)_3\text{SiOSi}(\text{C}_6\text{H}_5)_3 + \text{CO}_2 + \text{CO(NH}_2\text{H}_4)_2
\]

A study of the activity of the hydroxyl group of trimethylsilanol and triethylsilanol as compared to that of the hydroxyl group in tertiary organic alcohols is of
interest.

The reaction of metallic sodium with triethylsilanol dissolved in xylene is accompanied by the quantitative liberation of hydrogen (Bibl.15); while no hydrogen is liberated by the reaction with triethylcarbinol. After triethylsilanol is boiled 11 hours with alkali solutions, 90% of the trimethylsilanol still remains unreacted, and can easily be distilled. When a small quantity of concentrated HCl is added to triethylsilanol, hexaethyldisiloxane is obtained in 50% yield. Trimethylsilanol is converted to the dimer with considerably greater ease.

Table 67 gives the physical properties of various esters of trimethylsilanol and other derivatives of the trialkyl- and triarylsilanols.

Table 67

Physical Properties of Certain Derivatives of Trialkyl-(aryl)-silanols

<table>
<thead>
<tr>
<th>a) Name</th>
<th>b) Formula</th>
<th>c) M.p., °C</th>
<th>d) B.p., °C</th>
<th>e) Bibliography</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trimethylsodium-siloxane</td>
<td>(CH₃)₃SiONa</td>
<td>147-150</td>
<td>—</td>
<td>15</td>
</tr>
<tr>
<td>Triethylacetoxy-silane</td>
<td>(CH₃)₂SiOOCOCH₃</td>
<td>103</td>
<td>168</td>
<td>41</td>
</tr>
<tr>
<td>Triethylacetoxysilane</td>
<td>(C₂H₅)₂SiOOCOCH₅</td>
<td>—</td>
<td>214</td>
<td>41</td>
</tr>
<tr>
<td>Tripropylacetoxysilane</td>
<td>(C₃H₇)₂SiOOCOCH₇</td>
<td>—</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>Triphenylacetoxysilane</td>
<td>(C₆H₅)₂SiOOCOCH₅</td>
<td>—</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>Hexamethyldisiloxane-sulfate</td>
<td>[(CH₃)₂SiO]₂SO₂</td>
<td>45</td>
<td>—</td>
<td>41</td>
</tr>
<tr>
<td>Hexamethyldisiloxane-sulfate</td>
<td>[(C₆H₅)₂SiO]₂SO₂</td>
<td>—</td>
<td>170 (12 mm)</td>
<td>41</td>
</tr>
<tr>
<td>Hexamethyldisiloxane-phosphate</td>
<td>[(CH₃)₂Si]₂PO₄</td>
<td>86 (4 mm)</td>
<td>—</td>
<td>41</td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Melting point, °C; d) Boiling point, °C; e) Bibliography

**Organosilanediols**

The organosilanediols are the fundamental monomers of the substances whose polycondensation leads to the formation of linear polyorganosiloxanes of high molecular weight, or to cyclic products. This explains the exceptional importance of the or-
ganosilanediols in the synthesis of elastic high-molecular organosilicon compound.

Organosilanediols are most easily prepared by hydrolysis of alkyl- or aryl-chlorosilanes in an alkaline medium, or by hydrolysis of di-substituted esters of orthosilicic acid, and of dialkylacetoxy silanes:

\[
\begin{align*}
R_2SiCl_2 + 2H_2O & \rightarrow R_2Si(OH)_2 + 2HCl \\
R_2Si(OR)_2 + 2H_2O & \rightarrow R_2Si(OH)_2 + 2ROH \\
R_2Si(OOCCH_3)_2 + 2H_2O & \rightarrow R_2Si(OH)_2 + 2CH_3COOH
\end{align*}
\]

As a rule, processes of polycondensation also occur during the process of hydrolysis, so that up to now it has been possible to prepare only a limited number of representatives of the organosilanediols in the pure form, and even at that, in low yield.

The dialkylsilanediols are obtained only if the reaction is conducted cautiously, under mild conditions. Thus, for instance, on mixing an ether solution of diethyl dichlorosilane with 1.5N NaOH solution at a temperature not over 0°C, it is possible to prepare diethylsilanediol, boiling point 140°C, melting point 96°C. It is very labile, and condenses on distillation. It is soluble in water and oxygen-containing organic solvents (Bibl.16). In the pure form it is stable at room temperatures.

Depending on the conditions of hydrolysis, diphenyldichlorosilane may yield crystalline, amorphous, or oily products (Bibl.17).

To prepare tetraphenylhydroxysiloxane and hexaphenyldihydroxytrisiloxane, the partial hydrolysis of diphenyldichlorosilane is first effected. The incompletely hydrolyzed products are then separated and subjected to final hydrolysis.

**Partial Hydrolysis of Diphenyldichlorosilane.** In 1000 ml of ether 4 mols of diphenyldichlorosilane is dissolved, and a solution of 2 mols of water in 400 ml of dioxane is then added dropwise under vigorous stirring. After addition of the solution of water in dioxane, dry nitrogen is blown through the reaction mixture to remove the HCl. The solvents are distilled off, and the residue is fractionated under
reduced pressure. The fraction boiling at 238 - 241°C (1 mm) is redistilled, and then recrystallized from hexane. Tetraphenyldichlorodisiloxane crystallizes in waxy hexagonal prisms of melting point 38°C and boiling point 238 - 241°C (1 mm). The fraction boiling at 290 - 303°C (1 mm) contains a certain quantity of hexaphenyldichlorotrisiloxane mixed with hexaphenylcyclotrisiloxane. These two products are separated by extracting the hexaphenyldichlorotrisiloxane with heptane.

If 1.5 mol of diphenyldichlorosilane per mol of water are taken for hydrolysis, the yield of hexaphenyldichlorotrisiloxane is increased, while that of tetraphenyldichlorodisiloxane is reduced. At the same time the yield of hexaphenylcyclotrisiloxane is somewhat increased.

When the molar ratio between diphenyldichlorosilane and water is 1 : 1 or 0.67 : 1, polydiphenylhydroxysiloxane is not formed. In these cases the reaction product consists almost exclusively of hexaphenylcyclotrisiloxane. The formation of this compound in the products of partial hydrolysis indicates that monomeric diphenylsilanediol is formed by the hydrolysis of diphenyldichlorosilane, and subsequently undergoes condensation.

It may likewise be postulated that the formation of cyclic products is encouraged by the phenyl groups which are responsible for a position of the valence angle of the O - Si - O bond at which ring closure is facilitated.

Tetraphenyldichlorodisiloxane is hydrolyzed by the method that has been described for the preparation of diphenyldisilanol. The rate of hydrolysis of tetraphenyldichlorodisiloxane is an eighth of the rate of diphenyldichlorosilane. The hydrolysis may be accelerated somewhat by separating the water layer several times during the process and replacing it by fresh water. Tetraphenyldihydroxysiloxane may be recrystallized from a mixture of benzene and n-pentane. Its melting point is 113 - 114°C. The yield of product from 20 g of tetraphenyldichlorodisiloxane is 17 g, or 92% of theoretical.

Hexaphenyldichlorotrisiloxane is hydrolyzed by the method described for the pre-
paration of diphenylsilanediol (cf. p. 568). In this case the process of hydrolysis takes two days. Hexaphenyldihydroxytrisiloxane may be recrystallized from boiling pentane; melting point 111°C.

The fraction obtained on molecular distillation of the residue after the partial hydrolysis of diphenyldichlorosilane was subjected to hydrolysis, but no crystalline products could be obtained from it even under this treatment. Only oily products were obtained.

Table 68

Physical Properties of Dialkyl-(diaryl)-silanediols

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c) °C</th>
<th>d) °C</th>
<th>e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethylsilanediol</td>
<td>(CH₃)₂Si(OH)₂</td>
<td>100-101</td>
<td>96</td>
<td>10</td>
</tr>
<tr>
<td>Diethylsilanediol</td>
<td>(C₂H₅)₂Si(OH)₂</td>
<td>132</td>
<td>140</td>
<td>-</td>
</tr>
<tr>
<td>Diphenylsilanediol</td>
<td>(C₆H₅)₂Si(OH)₂</td>
<td>101</td>
<td>140-145</td>
<td>-</td>
</tr>
<tr>
<td>Dibenzylsilanediol</td>
<td>(C₆H₅)₂Si(OH)₂</td>
<td>123-124</td>
<td>113</td>
<td>116</td>
</tr>
<tr>
<td>Dicyclohexylsilanediol</td>
<td>C₆H₅(C₆H₁₁)₂Si(OH)₂</td>
<td>143</td>
<td>140-145</td>
<td>-</td>
</tr>
<tr>
<td>Phenylcyclohexylsilanediol</td>
<td>(C₆H₅)(C₆H₁₁)₂Si(OH)₂</td>
<td>70</td>
<td>71</td>
<td></td>
</tr>
<tr>
<td>tert-butylphenylsilanediol</td>
<td>C₆H₅(C₄H₉)Si(OH)₂</td>
<td>90</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Ethylbenzylsilanediol</td>
<td>C₆H₅(C₄H₉)CH₂Si(OH)₂</td>
<td>90</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>tert-butylmethyilsilanediol</td>
<td>CH₃(CH₃)₂(C₆H₅)Si(OH)₂</td>
<td>142</td>
<td>187</td>
<td>(740 mm)</td>
</tr>
<tr>
<td>tert-butylisocyanatophenylsilanediol</td>
<td>[(CH₃)₂C]C₆H₅Si(OH)₂</td>
<td>152</td>
<td>210</td>
<td>(740 mm)</td>
</tr>
<tr>
<td>tert-ethylisocyanatophenylsilanediol</td>
<td>[(CH₃)₂C]C₆H₅Si(OH)₂</td>
<td>82</td>
<td>123</td>
<td>(3 mm)</td>
</tr>
<tr>
<td>tert-dodecyloxyphenylsilanediol</td>
<td>[(CH₃)₂C]C₆H₅Si(OH)₂</td>
<td>10</td>
<td>45</td>
<td></td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Melting point, °C; d) Boiling point, °C;

Physical Properties

The dialkyldisilanols and diaryldisilanols are crystalline substances, readily soluble in many organic solvents; only dimethyl- and diethylsilanols are soluble in water. The dialkyldisilaneediols condense on long storage or heating, and gradually

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pass over into liquids of increasing viscosity, and then into resinous products.

Table 68 gives the melting points and boiling points of dialkyl-(diaryl)-silanediols.

**Chemical Properties**

Dimethylsilanediol and diethylsilanediol are soluble in water. Slight cleavage of water takes place on heating. Under the action of acids, even in the cold, they condense to form polymers. The diarylsilanediols are more stable, but even they are readily condensed. Thus, for instance, when 10 g of diphenylsilanol in 150 ml of ether is heated 3 hours in the presence of 5 ml of concentrated HCl, it is converted into hexaphenylcyclotrisiloxane. If 1 to 2 drops of an aqueous solution of an alkali are added to a boiling solution of diphenylsilanediol in 95% ethanol, octaphenylcyclotetrasiloxane is thrown down on cooling.

Diphenylsilanediol, according to various authors, has a melting point that varies according to the rate of temperature rise. Thus, at a rate of 2°C/minute, its melting point is 155°C, while it softens at 135°C. According to other data, diphenylsilanediol has a melting point of 132, 139, or 140°C. It can be easily recrystallized from hot ethanol, followed by precipitation by benzene. Treatment of a hot alcoholic solution of diphenylsilanediol with a small quantity of ammonia leads to the formation of the cyclical trimer. If a solution of diphenylsilanediol in methanol is allowed to stand for two weeks in the presence of 1 drop of concentrated HCl, a solid crystalline product is formed, which after recrystallization from a benzene-ethanol mixture has a melting point of 197 - 198°C. This product contains linear dimers and trimers. A certain quantity of cyclic trimer can also be separated from it by crystallization from a benzene-ethanol mixture in suitable proportions.

A solution of diphenylsilanediol in ethanol with a few drops of ammonia water forms a crystalline mass after standing 17 days. The melting point of the crystals is 161°C, and is not raised by recrystallization. Their molecular weight of 299 does not correspond to any condensation product of diphenylsilanediol.
The most interesting property of the silanediols is their exceptional power of condensing to form polymeric compounds, which are either of linear or cyclic structure, depending on the conditions. It has been established that polymers of cyclic structure may be converted into linear ones, and conversely. Thus cyclic polymers may be converted into linear polymers by the action of alkalies or acids on a solution of the polymer. Polymers of linear structure pass over into cyclic polymers on heating.

The condensation of silanediols under suitable conditions leads to the formation of polymers of molecular weight up to 50,000 - 70,000 or higher.

Cyclic compounds containing aromatic and aliphatic radicals are very stable substances, and are soluble in organic solvents; some of them have definite melting points, which increase as their structure becomes more complex. In mixtures with liquid, oily condensation products, some cyclic products form mixtures resembling vaseline.

Silanediols dissolve under the action of alkalies. They separate out of such solutions under the action of acids, which indicates their power to form salts. Many silanediols are condensed under the action of alkalies, however, and either do not form salts at all, or form them only on the end groups of the polymers.

Reagents such as acetyl chloride or phosphorus pentachloride chlorinate the silanediols.

Organosilanetriols

In view of the exceptional tendency of monomeric silanetriols to undergo polycondensation, even without heating, only two compounds have been isolated from them: phenylsilanetriol (Bibl.42) \( C_6H_5Si(OH)_3 \), melting point 180°C, and dichlorophenylsilanediol \( C_6H_5Cl_2Si(OH)_3 \), melting point 186°C, both of them obtained by me, in collaboration with A.A.Zhdanov, by hydrolysis of phenyl- and dichlorophenyltrichlorosilanes. In the very first stages of the synthesis, however, the organosilanetriols
form polymers in the form of viscous liquids, which harden into a glassy mass (Bibl. 1). To prepare space polymers, dialkyl- or diarylchlorosilanes or disubstituted esters of orthosilicic acid are ordinarily hydrolyzed together with alkyl- or aryltrichlorosilanes or mono-substituted esters in a single process.

According to the conditions under which the hydrolysis of trifunctional compounds is run, polymers of consistency ranging from viscous liquids to vitreous solids or powders are obtained. Products of a low degree of polycondensation are soluble in ether, benzene, acetone, dichloroethane, chlorobenzene, etc.; insoluble in water; and difficultly soluble in hot alkali, forming polymer salts.

When phenyltrichlorosilane is hydrolyzed by steam, a hard vitreous substance insoluble in the usual organic solvents is formed. On hydrolysis with weak cold ammonia water at 0°C, a mucilaginous product is formed, but if the hydrolysis is conducted at room temperature, then the product is obtained in the form of a powder that is poorly and only partially soluble in ether. Hydrolysis of phenyltrichlorosilane by aqueous KOH yields a solution of the corresponding salt, from which a resin is separated on treatment with CO₂ at 0°C. If the precipitation by CO₂ is carried out at room temperature, a precipitate only slightly soluble in ether is thrown down. Molecular weight determinations show that the most soluble fraction consists of 4 - 5-unit polymers. The less soluble fractions contain 6 - 7 units. On hydrolysis of the chloride by ice water (without using a solvent) most of the product remains in the solution. This shows that phenylsilanetriol, which is soluble in water, is formed as an intermediate product of hydrolysis. If an alkaline solution of phenylsilanetriol is neutralized, a gel is formed in a few hours. A mucilaginous product is separated from the ethereal solution obtained by extraction of the freshly acidified product by ether. Introduction of ammonium chloride into an alkaline solution of the product produces a white, flocculent precipitate, with very low solubility in ether (Bibl. 20).

On hydrolysis of benzyltrichlorosilane by steam, a white precipitate melting at
60 - 70°C is formed. Hydrolysis of propyltrichlorosilane by ice water gives a resin soluble in aromatic hydrocarbons, ether and other solvents. It is also soluble in alkanes, and the crystalline sodium salt can be isolated from this solution.

On hydrolysis of phenyltrichlorosilane, benzyltrichlorosilane, and naphthyltrichlorosilane, Koton obtained vitreous polymers (Bibl.21).

In isolated instances, with the object of preparing hard, brittle, insoluble and infusible polymers, hydrolysis of pure alkyl- or aryltrichlorosilanes or mono-substituted esters of orthosilicic esters is conducted.
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25. Dilthey, W. and Eduardoff, P. - Ber., 37, 1139 (1904)
31. Martin, G. - Ber., 45, 403 (1912)
   Moscow, Oborongiz (1949)
Silicon Compounds Containing Nitrogen

The organic silicon compounds containing nitrogen directly bound to the silicon constitute a rather extensive group of substances.

These compounds are distinguished by elevated thermal stability owing to the fact that the energy of the Si – N bond is greater than the energy of the Si – H and Si – C bonds, and is smaller only than the energy of the Si – O and Si – F bonds.

The nitrogen-containing organic silicon compounds may be divided into the following classes:

1. Alkyl-(aryl)-aminosilanes.
3. Alkyl-(aryl)-aminohalosilanes.
4. Alkyl-(aryl)-iminosilanes.
5. Alkyl-(aryl)-aminoalkylsilanes.
6. Silicon isocyanates.

To familiarize the reader with the properties of the nitrogen-containing inorganic compounds of silicon, which very often serve as the starting materials in the synthesis of nitrogenous organosilicon compounds, we give certain properties of the silicon nitrides and of the aminosilanes.
Silicon Nitrides

The silicon nitrides are prepared by roasting silicon in a current of nitrogen at 1300 - 1400°C and are of the composition: Si$_2$N$_3$, Si$_3$N$_4$, etc. (Bibl.1).

Silicon nitride, Si$_3$N$_4$, was first prepared as long ago as 1844, by roasting a mixture of silicon and potassium cyanide (Bibl.2). The brittle substance so obtained decomposes under the action of water, like all nitrides, forming ammonia and silicon dioxide:

$$\text{Si}_3\text{N}_4 + 6\text{H}_2\text{O} \rightarrow 3\text{SiO}_2 + 4\text{NH}_3$$

When a mixture of crystalline silicon and freshly calcined powdered coal is roasted in a current of nitrogen, a pale bluish mass of "silicon nitride" is formed (Bibl.4).

The method recommended for the industrial production of silicon nitrides is to heat a mixture of oxygen compounds of silicon and a metallic oxide, or iron, in a current of nitrogen (Bibl.3).

White, amorphous silicon nitride is also obtained by the action of ammonia on chlorosilanes (Bibl.5). This product does not melt at high temperatures, and does not change in air; it reacts with molten KOH to form ammonia and potassium silicate. Under the action of molten potassium carbonate on silicon nitride, potassium cyanate is formed, and with an excess of nitride, potassium cyanide as well.

Silicon nitride reacts energetically with Pb$_2$O$_4$ (taking fire); giving off nitrogen oxides.

When silicon nitride is roasted in a jet of nitrogen, carbonitrosilicon is formed (Bibl.6).

When a compound of the composition Si$_2$N$_3$H is heated to 1200 - 1400°C in a stream of nitrogen, the silicon nitride Si$_3$N$_4$ is formed:

$$3\text{Si}_2\text{N}_3\text{H} + 2\text{Si}_3\text{N}_4 + \text{N}_2$$
The nitride $\text{Si}_3\text{N}_4$ is white, the nitride $\text{SiN}$ is green (Bibl. 7).

The simplest nitride (the analog of cyanogen) is a polymeric product of composition $(\text{Si}_2\text{N}_2)_x$. It has been prepared on heating polymeric diimidoiminodisilane to $400^\circ\text{C}$ (Bibl. 8).

\[
\text{[HN} = \text{Si} - \text{Si} = \text{NH}]_x \rightarrow [\text{Si}_3\text{N}_4]_x + x\text{NH}_3.
\]

In spite of the great thermal stability of the polymer so formed, its high sensitivity to oxygen is characteristic of this compound. Simple contact with moist air is sufficient to decompose it. The process is accompanied by strong heating and evolution of ammonia. Such polymeric compounds have little described in the literature. There are only references to the existence of polymeric compounds of the type $(\text{Si}_2\text{N}_2)_x$.

All silicon nitrides are white or green solids, powders or brittle substances. All of them are highly refractory.

The nitrides $\text{Si}_3\text{N}_4$, $\text{SiN}$, and $(\text{Si}_2\text{N}_2)_x$ are unaffected by dilute mineral acids. HF decomposes them with difficulty. Steam, even at $800^\circ\text{C}$, acts only slightly on some nitrides. The heat of formation of $\text{Si}_3\text{N}_4$ is $159.3$ kcal. The manufacture of silicon cyanides and cyanamides from silicon nitrides has recently been proposed (Bibl. 9). The nitrides today, however, are not of great industrial importance.

The nitrides of silicon have been little studied. The data in the literature are very contradictory. This is true of the composition and structure of the silicon nitrides and of their chemical stability. Many works state that they are sensitive to moisture and acids; others assert the opposite. This is probably to be explained by the fact that different investigators have characterized products of different degrees of polymerization, containing not only nitrogen but also hydrogen, for instance compounds of the type of diimidoiminodisilane.
\[
\begin{equation}
\left[ \text{HN} \rightarrow \text{Si} \rightarrow \text{Si} \rightarrow \text{NH} \right]
\end{equation}
\]

as individual nitrides of silicon.

**Aminosilanes**

The aminosilanes are obtained from the corresponding halogen compounds of silicon and ammonia or amines.

This class includes the compounds:

- \( \text{SiH}_3\text{NH}_2 \) monoaminosilane
- \( \text{SiH}_2(\text{NH}_2)_2 \) diaminosilane
- \( \text{SiH}(\text{NH}_2)_3 \) triaminosilane
- \( \text{Si}(\text{NH}_2)_4 \) tetraaminosilane

Monoaminosilane and tetraaminosilane have been rather well studied. Diaminosilane and triaminosilane have not yet been isolated in monomeric form.

The aminosilanes, like the organic amines, may have primary, secondary and tertiary amino groups:

- \( \text{SiH}_3\text{NH}_2 \) monoaminosilane
- \( (\text{SiH}_3)_2\text{NH} \) aminodisilane
- \( (\text{SiH}_3)_3\text{N} \) aminotrisilane

Aminosilanes are easily prepared by the action of ammonia on monochlorosilane.

According to the quantities of the reacting substances, different compounds of the aminosilane series are obtained. With an excess of ammonia, both solid and gaseous compounds are formed. The reaction proceeds best of all when an excess of monochlorosilane is used:

\[ 3\text{SiH}_3\text{Cl} + 4\text{NH}_3 = (\text{SiH}_3)_3\text{N} + 3\text{NH}_4\text{Cl} \]

The formation of aminosilanes is believed to proceed in several stages.
At first, aminosilane \((\text{SiH}_3)_2\text{NH}\) is obtained in predominating quantity, followed by monoaminosilane \(\text{H}_2\text{SiNH}_2\) and aminotrisilane \((\text{H}_3\text{Si})_3\text{N}\).

The reaction proceeds according to the following mechanism:

\[
\begin{align*}
2\text{H}_4\text{SiCl} + 3\text{NH}_3 & \rightarrow (\text{H}_3\text{Si})_2\text{NH} + 2\text{NH}_4\text{Cl} \\
\text{H}_3\text{SiCl} + 2\text{NH}_3 & \rightarrow \text{H}_2\text{SiNH} = \text{NH} + \text{NH}_4\text{Cl} \\
3\text{H}_4\text{SiCl} + 4\text{NH}_3 & \rightarrow (\text{H}_3\text{Si})_3\text{N} + 3\text{NH}_4\text{Cl}
\end{align*}
\]

Dichlorosilane reacts with an excess of ammonia at normal temperatures to form polymeric products:

\[
\begin{align*}
\text{SiH}_2\text{Cl} + 3\text{NH}_3 & \rightarrow \text{H}_2\text{Si} = \text{NH} + 2\text{NH}_4\text{Cl} \\
\text{XH}_3\text{Si} = \text{NH} & \rightarrow (\text{H}_3\text{Si})_x
\end{align*}
\]

The degree of polymerization of the product is found to be 7 to 8 (determined by the lowering of the freezing point in benzene). The presence of products of a greater degree of polymerization is also possible.

Aminodisilane \((\text{SiH}_3)_2\text{NH}\), by cleavage of \(\text{SiH}_2\text{NH}\), is evidently able to be converted into aminosilane \(\text{SiH}_2\text{NH}\), which, like \(\text{CH}_2\text{NH}\), has not been isolated in the monomeric state. Aminosilane is thus transformed into various polymeric products.

Tetraaminosilane is obtained by the action of ammonia on halogen compounds of silicon:

\[
\text{SiCl}_4 + 6\text{NH}_3 \rightarrow \text{Si(NH}_4)_4 + 4\text{NH}_4\text{Cl}
\]

Tetraaminosilane was first prepared by Longfeld (Bibl.10) by the reaction of \(\text{SiCl}_4\) with ammonia in an atmosphere of dry nitrogen.

**Preparation of Tetraaminosilane.** A benzene solution of ammonia is mixed with \(\text{SiCl}_4\) in an apparatus filled with dry nitrogen, carefully protected against the access of air and moisture. The flocculent white powder formed is transferred by means of a nitrogen jet into a large receiver. A separating funnel may be used for this purpose. A layer of cotton wool is placed in the receiver (at the narrow end), and the precipitate is washed with benzene or ligroin. The apparatus must be so
mounted that the washing can be done without access of air. The receiver is provided with a jacket for hot water, and is connected to a pump, which aspirates a stream of nitrogen over the precipitate. The reaction is conducted at 80 - 90°C, under pressure of 25 - 30 mm. After washing, the precipitate is dried. The final removal of the solvent is accomplished by grinding the precipitate to powder and a second drying under reduced pressure.

**Determination of Silicon.** The silicon content of the compound so obtained is determined by treatment with fuming nitric acid and weighing the silicon dioxide.

**Determination of Chlorine.** To determine the quantity of admixture of chlorine-containing compounds in the tetraaminosilane, it is added to an aqueous solution of nitric acid and silver nitrate, and the mixture is allowed to stand overnight.

The precipitate thrown down is dissolved in KCN, and the silver is then deposited electrolytically, or dissolved in ammonia, again precipitated with nitric acid, and then converted into silver chloride.

**Determination of Nitrogen.** The nitrogen is determined by two methods:

(a) decomposition by water, followed by titration of the ammonia:

\[
\text{Si(NH}_4\text{)}_4 + 4\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 + 4\text{NH}_3
\]

(b) decomposition with NaOH, followed by titration of the ammonia:

\[
\text{Si(NH}_4\text{)}_4 + 4\text{KOH} \rightarrow \text{Si(OK)}_4 + 4\text{NH}_3
\]

In the former case the nitrogen split off by the water is determined, in the latter case, the total nitrogen.

Tetraaminosilane has also been prepared by other authors, by reacting SiCl\textsubscript{4} with ammonia below 0°C (Bibl.11).

Tetraaminomonosilane is a full amide of orthosilicic acid. It is a white, amorphous substance, unstable above 0°C. It is easily decomposed by water into ammonia and silicon dioxide.
Si(NH)₄ + 2H₂O → SiO₂ + 4NH₃

At temperatures above 0°C, tetraaminomonosilane is converted into a more stable compound, imidosilane Si(NH)₂.

Aminotrisilane (H₂Si)₃N is a mobile colorless liquid, which explosively takes fire in air, giving off white and brown oxidation products. It remains unchanged in the absence of air, and retains its monomeric form. Aminotrisilane is highly volatile; its vapor pressure at -80°C is 0.1 mm, at 0°C it is 109 mm, and at 15°C, 212 mm.

Aminotrisilane is very sensitive to water, and is decomposed by it, giving off hydrogen and ammonia:

\[(H₂Si)₃N + 6H₂O = 3SiO₂ + NH₄ + 9H₂\]

Aminomonosilane SiH₃NH₂ and aminodisilane (SiH₃)₂NH are still more volatile than aminotrisilane, and it is very difficult to isolate them.

The aminosilanes differ from the organic amines in their behavior to HCl. It is well known that the methylamines add HCl to form the corresponding salts.

The aminosilanes do not form salts, but under the action of HCl, even at room temperature, they form the original chlorosilane.

\[
\begin{align*}
\text{SiH₃NH₂ + 2HCl} & \rightarrow \text{SiH₃Cl + NH₄Cl} & (1) \\
\text{(SiH₃)₂NH + 3HCl} & \rightarrow 2\text{SiH₃Cl + NH₄Cl} & (2) \\
\text{(SiH₃)₂N + 4HCl} & \rightarrow 3\text{SiH₃Cl + NH₄Cl} & (3) \\
\text{SiH₂NH + 3HCl} & \rightarrow \text{SiH₂Cl₂ + NH₄Cl} & (4)
\end{align*}
\]

Reactions (1), (2) and (3) proceed easily and give almost theoretical yields. Reaction (4) proceeds with greater difficulty, and is accompanied by various intermediate and side reactions.

Under the action of HCl on the polymeric compound SiH₃(NH)ₓ on heating, SiHCl₃ is formed. Under the action of HI, SiHI₃ is formed. It is highly probable that the iodides SiH₃I and SiH₂I₂, which are still unknown, may be obtained from polymeric compounds of this type by the action of HI.
**Alkyl-(aryl)-aminosilanes**

When halogen atoms in alkyl-(aryl)-halosilanes are replaced by an amino group, the following series of compounds can be prepared:

\[ \text{RSi(NH}_2\text{)}_n; \quad \text{R}_2\text{Si(NH}_2\text{)}_n; \quad \text{R}_3\text{SiNH}_2; \quad \text{(R}_3\text{Si)}_2\text{NH}. \]

Replacement of the hydrogen atoms in the amino groups of these compounds by alkyl or aryl radicals gives a series of alkyl-(aryl)-substituted alkyl-(aryl)-aminosilanes of the type \( \text{R}_3\text{SiNH}_2, \text{R}_3\text{SiNR}_2, \) etc.

Compounds of the type \( \text{R}_3\text{SiNH}_2, \text{(R}_3\text{Si)}_2\text{NH} \) were first prepared as far back as 1907 (Bibl.12). They have been studied in detail, however, only at a relatively recent date.

**Preparation of Alkyl-(aryl)-aminosilanes**

Alkyl-(aryl)-aminosilanes of the type \( \text{R}_3\text{SiNH}_2 \) are prepared by the action of ammonia on the corresponding alkyl- or arylchlorosilanes. The first representative of this series, trimethylaminosilane, \( \text{(CH}_3\text{)}_3\text{SiNH}_2 \), in spite of numerous attempts, has not yet been isolated (Bibl.13). Other compounds of this series, triethylaminosilane, \( \text{(C}_2\text{H}_5\text{)}_3\text{SiNH}_2 \), and triphenylmethyldiminosilane, \( \text{(C}_6\text{H}_5\text{)}_3\text{SiNH}_2 \), have, however, been prepared.

The behavior of the alkylaminosilanes, of the type \( \text{R}_3\text{SiNH}_2 \), recalls that of the corresponding hydroxy-silanes \( \text{R}_3\text{SiOH} \). The lowest representatives of these classes of compounds are characterized by easy cleavage of ammonia or water to form the corresponding dimers.

When ammonia acts on trimethylchlorosilane, hexamethylaminodisilane \( \text{[(CH}_3\text{)}_3\text{Si]}_2\text{NH} \) is formed instead of the expected trimethylaminosilane (Bibl.13).

**Preparation of Hexamethylaminodisilane.** In a round-bottomed flask, provided with a fractionating column and a side tube, is placed a solution of 109 g of trimethylchlorosilane, of boiling point 57.1 - 57.3°C (750 mm), in 500 cm³ of dry ether,
and ammonia is passed in through the side tube. Immediately on introduction of the ammonia, a white precipitate appears, and a slight heating of the mixture is observed. The mixture is then heated to the fractionating temperature, and the passage of the stream of ammonia is continued slowly for 6 hours. The ammonium chloride is precipitated, and the ethereal solution is decanted and filtered. A powdery white precipitate is obtained, which is washed with three 50 cm$^3$ portions of dried ether.

The ether is distilled off, and the product is then fractionated in a rectification column with 10 - 12 theoretical plates, yielding 23.4 g of hexamethyldiaminodisilane; boiling point 125.4 - 125.6°C, refractive index $n_2^0 = 1.4080$, specific gravity 0.7724 (vacuum).

Trimethylmethyldiaminodisilane, with boiling point 70°C (747 mm), and trimethylethylaminodisilane, with boiling point 91°C (747 mm), are similarly prepared. The latter forms an azotropic mixture of boiling point 90.6°C with trimethylsilanol and hexamethyldisiloxane.

Trimethylmethyldiaminodisilane is prepared by the action of diethylamine on trimethylchlorosilane; boiling point 126.5°C (750 mm).

These compounds are slowly decomposed by water and by alkali, forming trimethylsilanol, but in the presence of dilute acid or aqueous alcohol, hydrolysis proceeds very readily. They do not react with metallic sodium, like the organic azines or amines, but they do react with methylmagnesium iodide by the Tserevitinov reaction, evolving methane.

Triethylaminodisilane (Bibl.14), $(C_2H_5)_3SiNH_2$, is easily prepared by the reaction of ammonia with triethylchlorosilane:

\[ R_3SiX + 2NH_3 \rightarrow R_3SiNH_2 + NH_4X \]

At the same time, hexaethylaminodisilane, $(C_2H_5)_3SiNHSi(C_2H_5)_3$, is formed in considerable quantities.

Under the action of HCl or HI, concentrated hydrochloric acid, concentrated
hydrofluoric acid, or a mixture of sulfuric and hydrobromic acids, on trialkylamino-silanes, the corresponding halosilanes are found:

Thus the trialkylaminosilanes may be an intermediate product in the synthesis of certain trialkylhalosilanes from trialkylchlorosilane.

Preparation of triethylaminosilane. In a three-necked 200 ml flask with a reflux condenser, a dropping funnel, and a stirrer with mercury seal, 100 ml of liquid ammonia is placed. The flask is placed in a bath containing a mixture of dry ice and acetone, and 75 g of triethylchlorosilane is introduced into the liquid ammonia from the dropping funnel, with stirring, over a period of 30 min. After stirring for an hour, the excess ammonia is evaporated off, and the reaction mass is diluted with ether. The precipitate of ammonium chloride is filtered off, and the ether is distilled off. The reaction product is fractionated in a column packed with glass spirals and having 20 theoretical plates, yielding 46 g of triethylaminosilane; boiling point 134°C. The yield is 70% of theoretical.

Preparation of Amno-α-chloroethyl(diethyl)silane. To 100 ml of liquid ammonia 93 g of α-chloroethyl(diethyl)chlorosilane is added as indicated above, yielding 72 g (0.44 mol) of α-chloroethyl(diethyl)aminosilane; boiling point (38 mm) 93°C; refractive index nD = 1.4570; specific gravity d = 0.9604. The yield is 88% of theoretical.

Reaction of a Trialkylaminosilane with Concentrated HCl. In a 200 ml three-necked flask with a reflux condenser, dropping funnel, and stirrer with mercury seal, 160 ml of concentrated HCl is placed. The flask is cooled in an ice bath, and 13 g of triethylaminosilane is added to the HCl. After 30 minutes of stirring, the reaction mixture is transferred to a separating funnel, and the upper layer is taken off. This layer is dried over sodium sulfate and distilled, yielding 12 g of triethylchlorosilane; boiling point 144 - 154°C, specific gravity d = 0.8977. The yield is 80% of theoretical.
α-Chloroethyldiethylaminosilane reacts with HCl by the same method. For the reaction, 13 g of α-chloroethyldiethylaminosilane and 160 ml of HCl are taken.

**Reaction of Triethylaminosilane with Hydrofluoric Acid.** In a 200 ml flask, 60 ml of 48% HF is placed. The flask is cooled on an ice bath, and 12 g of triethylaminosilane is added over a period of 5 minutes. The reaction mixture is stirred 10 minutes, then the upper layer is separated in a separating funnel and dried with sodium sulfate. Distillation yields 10.5 g of triethylfluorosilane; boiling point 109 - 110°C; specific gravity d = 0.8380. The yield is 89% of theoretical.

The reaction of 11 g of α-chloroethyldiethylaminosilane with 60 ml of 48% HF by the above method yields 9 g of α-chloroethyldiethylfluorosilane; boiling point 149 - 150°C; specific gravity d = 0.9961. The yield is 82% of theoretical.

**Reaction of Triethylaminosilane with Hydrogen Chloride.** In a 200 ml three-necked flask provided with a reflux condenser, stirrer with mercury seal, and gas inlet tube, 150 ml of dry ether and 20 g of triethylaminosilane are placed. Hydrogen chloride is passed into the mixture through the gas inlet tube until the mixture is completely saturated. The ammonium chloride is filtered off, and the ether is distilled off on the water bath. Distillation of the residue (after removal of the ether) yields 16 g of triethylchlorosilane; boiling point 143 - 145°C; specific gravity d = 0.8974. Yield: 70% of theoretical.

A solution of 18 g of α-chloroethyldiethylaminosilane in ether is treated with dry HCl as described above, yielding 15.5 g of α-chloroethyldiethylchlorosilane; boiling point 179 - 181°C; specific gravity d = 1.0385; refractive index n = 1.1153. Yield, 78% of theoretical.

**Reaction of Triethylaminosilane with HBr.** An ethereal solution of 39 g of triethylaminosilane in 150 ml of ether is treated with dry HBr by the method described above, yielding 41.5 g of triethylbromosilane; boiling point 162 - 163°C; refractive index n = 1.4563; specific gravity d = 1.1403. The yield is 70% of theoretical.

An ethereal solution (24 g) of α-chloroethyldiethylchlorosilane is treated, as
above, with dry HBr, yielding 12 g of \( \alpha \)-chlooroethyldiethylbromosilane; boiling point 194 - 196°C; refractive index \( n_D = 1.4762 \). Yield, 26% of theoretical.

Products of a higher degree of purity are formed by the reaction of the corresponding aminosilanes with a mixture of sulfuric and hydrobromic acids.

**Reaction of Aminosilanes with a Mixture of Sulfuric and Hydrobromic Acids.** Into a 1-liter three-necked flask provided with a reflux condenser, a stirrer with mercury seal, and a dropping funnel, 300 ml of 48% HBr is poured. The flask is cooled on a water bath with ice, and 200 ml of conc. \( \text{H}_2\text{SO}_4 \) is poured into it. Then 41 g of triethylaminosilane is added from a dropping funnel to the mixture of acids. After stirring the reaction mixture 20 minutes, the two layers that form are separated, and the organic upper layer is dried with sodium sulfate. Fractionation yields 33.5 g of triethylbromosilane; boiling point 78 - 79°C (45 mm); refractive index \( n = 1.4561 \). The yield is 55% of theoretical.

\( \alpha \)-Chloroethyldiethylbromosilane is prepared by the above method from 52 g of \( \alpha \)-chloroethylaminosilane. Distillation of the reaction products yields 58.5 g of \( \alpha \)-chloroethyldiethylbromosilane; boiling point 105 - 106°C (46 mm); specific gravity \( d_4 = 1.2661 \). The yield is 81% of theoretical.

Triphenylaminosilane, \( (\text{C}_6\text{H}_5)_3\text{SiNH}_2 \), was prepared somewhat earlier from triphenylchlorosilane and ammonia in the presence of an excess of sodium.

\[
\text{Na} \quad (\text{C}_6\text{H}_5)_3\text{SiCl} + 2\text{NH}_3 \xrightarrow{\text{Na}} (\text{C}_6\text{H}_5)_3\text{SiNH}_2 + \text{NH}_4\text{Cl}
\]

When an excess of \( \text{SiCl}_4 \) reacts with an organic amine, the corresponding amino derivative and an equivalent of amine hydrochloride are formed. The reaction is very energetic. In this way, diphenylaminochlorosilane, di-\( \alpha \)-methylphenylaminochlorosilane, dimethylphenylaminochlorosilane, and di-\( \alpha \)-naphthylaminochlorosilane may be prepared.

Hydrolysis of the products so obtained by water gives silicic acid and the amine hydrochloride.
Compounds containing a tertiary nitrogen atom—pyridine or quinoline—form addition products with SiCl₄ (Bibl.15): (C₅H₅N)₂·SiCl₄ and (C₇H₇N)₂·SiCl₄. On the action of an excess of aniline, o-toluidine or β-naphthylamine of SiCl₄, tetraphenylaminosilane, tetra-o-tolylaminosilane, and tetra-β-naphthylaminosilane are formed, respectively (Bibl.16).

The action of p-toluidine on benzylpropylethylchlorosilane yields an amino derivative:

\[
\begin{align*}
\text{CH}_3 & + \text{SiCl}_4 \rightarrow [\text{C}_9\text{H}_7\text{SiH}_3\text{C}_9\text{H}_7\text{CH}_2\text{CH}_3] + \text{HCl}
\end{align*}
\]

Stock and Somieski (Bibl.17) prepared derivatives of chlorosilane, containing nitrogen attached to the silicon, by treating chlorosilane with ammonia. Emilis and Miller (Bibl.18) prepared methylaminodisilane and ethylaminodisilane by reacting methyl- or ethylamine with chlorosilane.

When triphenylchlorosilane and lithium react in ethylamine solution, the free triphenyl radical is formed (Bibl.19) and adds to the ethylamine, separating in the form of a crystalline compound of melting point 45°C.

\[
\begin{align*}
\text{[(C₆H₅)₃Si]Br} + 1.5 \cdot \text{C}_₂\text{H}_₅\text{NH}_₂ & \rightarrow [\text{C}_₉\text{H}_₇\text{SiH}_₃\text{C}_₉\text{H}_₇\text{CH}_₂\text{CH}_₃] + \text{LiBr} \\
\end{align*}
\]

Triphenylaminoethylsilane reacts with lithium to give the lithium derivative of triphenylsilane. When triphenylaminoethylsilane is heated or allowed to stand, it is converted into hexaphenylaminodisilane and ethylamine.

Reynolds (Bibl.20, 21) studied the reaction between thiourea and SiBr₄. Addition products of the following composition are formed as a result of this reaction: \([\text{CS(NH}_₂)_₂]·(\text{SiBr}_₄)\). Phenylthiourea and allylthiourea react similarly. Treatment of the addition products with ethanol forms tetraethoxysilane, diethyl isocyanatobromide and certain other substances whose composition has not been established.
On the reaction of potassium amide with triethylsilane, hexaethylaminodisilane is formed (Bibl.22).

Hexaethylaminodisilane can be prepared more simply by the action of ammonia on trimethylchlorosilane or on hexamethylsulfonodisilane (Bibl.23). Hexamethylaminodisilane is hydrolyzed by water with relative ease to form trimethylsilanol (Bibl.14). It does not react with metallic sodium, but does form magnesium derivatives:

$$(\text{CH}_3)_3\text{SiNHSi(CH}_3)_3 + \text{CH}_3\text{MgJ} \rightarrow (\text{CH}_3)_3\text{SiN(MgJ)Si(CH}_3)_3 + \text{CH}_4$$

Products containing organic radicals attached to the silicon atom may be prepared in the following way:

$$(\text{CH}_3)_3\text{SiCl} + \text{CH}_3\text{NH}_2 \rightarrow (\text{CH}_3)_3\text{SiNHCH}_3 + \text{HCl}$$

$$(\text{CH}_3)_3\text{SiCl} + (\text{CH}_3)_3\text{SiNHCl}_3 \rightarrow (\text{CH}_3)_3\text{SiN(CH}_3)_3 + (\text{CH}_3)_3\text{SiHCN} + \text{HCl}$$

In the same way $(\text{CH}_3)_3\text{SiNHCH}_3$; $(\text{CH}_3)_3\text{SiN(C}_2\text{H}_5)_2$; $(\text{C}_2\text{H}_5)_3\text{SiNH}_2$; and $(\text{C}_2\text{H}_5)_2(\text{CH}_3\text{CHCl})\text{SiNH}_2$ have been prepared (Bibl.24).

Under the action of HCl on $(\text{CH}_3)_3\text{SiNHCH}_3$, trimethylmethy氨基silane, the cleavage of methyamine hydrochloride and the formation of trimethylchlorosilane have been observed (Bibl.25).

$$(\text{CH}_3)_3\text{SiNHCH}_3 + 2\text{HCl} \rightarrow (\text{CH}_3)_3\text{SiCl} + \text{CH}_3\text{NH}_2\cdot\text{HCl}$$

Ammonolysis of triphenylchlorosilane by liquid ammonia yields colorless triphenylaminosilane, melting point 55 - 56°C, which is isolated by extraction with petroleum ether.

Alkylaminosilanes of the type $R_2\text{SiNH}$ and $R_3\text{SiNR}_2$ are obtained by means of the ammonolysis reaction, that is, by the action of the corresponding amines on alkylhalodisilanes (Bibl.18):

$$R_2\text{SiCl} + \text{RNH}_2 \rightarrow R_2\text{SiNH} + \text{HCl}$$

$$R_2\text{SiCl} + R_2\text{NH} \rightarrow R_3\text{SiNR}_2 + \text{HCl}$$
Methylaminotrimethylsilane has been prepared in this way.

Preparation of Methylaminotrimethylsilane. 1. In a round-bottomed liter flask provided with a reflux condenser a solution of 54 g of trimethylchlorosilane in 500 cc of anhydrous ether is placed. An excess of anhydrous methylamine is introduced through a side tube. Yield, 19.7 g (38%) of methylaminotrimethylsilane; boiling point 71°C (755 mm); refractive index n20 = 1.3905; specific gravity d4 20 = 0.7395. Together with this, 12.7 g of hexamethyldisiloxane is also formed.

2. In a 2-liter unsilvered Dewar vessel, provided with a cork stopper, a stirrer, and an additional funnel, 200 g of anhydrous liquid methylamine is placed, and 217 g of trimethylchlorosilane is added to it, with stirring. After half of the total quantity of trimethylchlorosilane has been used, the reaction mixture solidifies. After adding the entire quantity of trimethylchlorosilane, the solid substance is broken up, shaken with ether, and suction-filtered. The filtrate is fractionated, yielding 114.5 g (55%) of methylaminotrimethylsilane. The filtration residue (130.5 g) after vacuum distillation (0.1 mm) is a white solid.

Ethylaminotrimethylsilane and diethylaminotrimethylsilane are prepared similarly.

From 108.5 g of trimethylchlorosilane dissolved in 500 cm3 of absolute ether, 29.2 g (25%) of ethylaminotrimethylsilane, (CH3)3SiNCH2H5, was obtained, with an azeotropic mixture of trimethylsilanol and hexamethyldisiloxane as an impurity.

Diethylaminotrimethylsilane, (CH3)3SiN(C2H5)2, is obtained on addition of a solution of 54.0 g of trimethylchlorosilane in 500 cm3 of absolute ether to a mixture of 80 g of diethylamine and 1000 cm3 of absolute ether. Diethylaminotrimethylsilane has a boiling point of 126-126.5°C (750 mm); refractive index nD 20 = 1.4112. The yield is 28% of theoretical. Hexamethyldisiloxane (10.5 g) is also obtained.

Methylaminodisilane is easily prepared by reaction of monochlorosilane and methylamine (Bibl.18):

$$3CH_3NH_2 + 2SiH_4Cl \rightarrow CH_3N(SiH_3)_2 + 2CH_3NH_2-HCl$$

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Methylaminodisilane, $\text{CH}_3\text{N(SiH}_3\text{)}_2$, is a liquid that is stable in air, with a boiling point of 32.3°C. It is, however, readily hydrolyzed by alkali.

The behavior of this compound differs from that of organic amines, in its quantitative decomposition under the action of HCl.

$$\text{CH}_3\text{N(SiH}_3\text{)}_2 + 3\text{HCl} \rightarrow 2\text{SiH}_4\text{Cl} + \text{CH}_2\text{NH}_2\cdot\text{HCl}$$

Ethylaminodisilane, $\text{C}_2\text{H}_5\text{N(SiH}_3\text{)}_2$, is prepared similarly. It is a liquid, with a boiling point of 65.9°C. Its properties resemble those of methylaminodisilane.

Dimethylamine and monochlorosilane react even at room temperature to form dimethylaminomonosilane, $(\text{SiH}_3)\text{N(CH}_3\text{)}_2$. This compound forms an unstable salt with any excess of monochlorosilane.

Trimethylamine and monochlorosilane react in the cold, forming a solid addition product, $\text{N(CH}_3\text{)}_3\cdot\text{SiH}_3\text{Cl}$. This product differs from the analogous organic compounds by being instantaneously decomposed by water to form trimethylamine, HCl and disiloxane, $(\text{SiH}_3)_2\text{O}$. It is hydrolyzed by alkalies according to the equation:

$$\text{N(CH}_3\text{)}_3\cdot\text{SiH}_3\text{Cl} + 3\text{NaOH} \rightarrow \text{Na}_2\text{SiO}_3 + \text{NaCl} + \text{N(CH}_3\text{)}_3 + 3\text{H}_2$$

On dissociation of the salt a pressure of 9 mm arises at 20°C. When the temperature is increased to 91°C, this pressure goes up to one atmosphere. $\text{N(CH}_3\text{)}_3\cdot\text{SiH}_3\text{Cl}$ reacts with alcohols to form volatile esters:

$$\text{C}_2\text{H}_5\text{OH} + \text{N(CH}_3\text{)}_3\cdot\text{SiH}_3\text{Cl} \rightarrow \text{SiH}_3\text{OC}_2\text{H}_5 + \text{N(CH}_3\text{)}_3\cdot\text{HCl}$$

The series of quaternary salts given below is arranged in order of decreasing stability.

- $\text{N(CH}_3\text{)}_4\text{Cl}$ - stable
- $\text{N(SiH}_3\text{)}_2(\text{CH}_3\text{)}_2\text{Cl}$ - moderately stable
- $\text{N(SiH}_3\text{)}_2(\text{CH}_3\text{)}_2\text{Cl}$ - unstable
- $\text{N(SiH}_3\text{)}_3(\text{CH}_3\text{)}\text{Cl}$ - not formed
Kraus and Nelson have prepared hexaethylaminodisilane, \([\text{C}_2\text{H}_5]_3\text{Si}]_2\text{NH}\), by the action of ammonium bromide on the potassium salt of hexaethylaminodisilane in a liquid ammonia medium (Bibl. 22).

When, for instance, triphenylmethane is treated with sodium amide or potassium amide dissolved in ammonia, the potassium derivative of triphenylmethane is formed, and ammonia is given off:

\[
\text{(C}_6\text{H}_5)\text{CH} + \text{KNH}_2 \rightarrow \text{(C}_6\text{H}_5)\text{CK} + \text{NH}_3
\]  

(1)

A different reaction is observed in the case of triethylsilane. Triethylsilane reacts with potassium amide in liquid ammonia to form the potassium derivative of hexaethylaminodisilane, giving off hydrogen:

\[
2\text{(C}_3\text{H}_8)\text{SiH} + \text{KNH}_2 \rightarrow \text{[(C}_3\text{H}_8)\text{Si}]_2\text{NK} + 2\text{H}_2
\]  

(2)

Ethylaminotriethylsilane, \([\text{C}_2\text{H}_5]_3\text{SiNHCH}_2\text{H}_5\), is prepared by the action of lithium on a solution of triethylsilane and ethylamine (Bibl. 22). By analogy with the organic compounds, it might be expected that the alkali metals would react with triethylsilane in ammonia or ethylamine solution according to the equation:

\[
\text{(C}_3\text{H}_8)\text{SiH} + \text{Li} = \text{(C}_3\text{H}_8)\text{SiLi} + \frac{1}{2}\text{H}_2
\]  

(3)

Such a reaction has in fact been observed in the case of triphenylmethane dissolved in ammonia.

In view of the very low solubility of triethylsilane in ammonia, ethylamine was used as the solvent. Lithium is rather well soluble in it. It was found, however, that twice as much hydrogen was formed as was called for by eq. (3). This indicates that metallic lithium, as a catalyst, participates only indirectly in the reaction, which may be represented as follows:
This reaction is homogeneous; its velocity increases with the quantity of lithium taken in the reaction.

Ethylaminotriethylsilane is a colorless liquid with a sharp odor of camphor. It is soluble in ethylamine and is easily distilled in a vacuum; it does not react with lithium in ethylamine solution. It may also be prepared from triethylbromosilane and ethylamine in the presence of lithium, forming one equivalent of hydrogen per mol of starting bromide.

\[
(C_2H_5)_3SiBr + C_2H_5NH_2 + Li = (C_2H_5)_3SiNH(C_2H_5)_2 + LiBr + \frac{1}{2} H_2
\]

The compound obtained as a result of this reaction was identical with the compound prepared from triethylsilane and ethylamine in the presence of lithium.

Hexaphenylaminodisilane, \([(C_6H_5)_3Si]_2NH\), is prepared by reacting triphenylsilane with liquid ammonia in the presence of sodium.

It is a crystalline substance with a melting point of 175°C, which is very stable in air and even against the action of boiling dilute NaOH. It crystallizes well from alcoholic solution, but is readily hydrolyzed in the presence of HCl, forming triphenylsilanol. The mechanism of the reaction by which hexaphenylaminodisilane is formed has not been described. Its formation obviously involves the formation of an intermediate sodium derivative of triphenylsilane, followed by an exchange reaction between this compound and ammonia:

\[
(C_6H_5)_3SiH + Na \rightarrow (C_6H_5)_3SiNa + \frac{1}{2} H_2
\]

\[
2(C_6H_5)_3SiNaNH + NH_3 \rightarrow (C_6H_5)_3SiNH\text{Si}(C_6H_5)_3 + 2Na + H_2
\]

Such reactions may be accompanied by the formation of triphenylaminodisilanes or their hydrolysis products. The authors have observed the formation of resinous products together with crystalline compounds corresponding in composition to hexaphenylaminodisilane.
disilane, which however, were not further investigated.

The tetraaminosilanes of type Si(NHR)$_4$ and the diaminosilanes of type Si(NR)$_2$ have been studied in greater detail. Tetraethylaminosilane has been prepared by the reaction of ethylamine and SiCl$_4$ (Bibl.10). The reaction is conducted in ligroin. On cooling the reaction mass with ice water, ethylamine hydrochloride is at once thrown down and filtered off from the solution. The part of the product dissolved in the ligroin contains tetraethylaminosilane. The reaction follows the equation

$$\text{SiCl}_4 + 8\text{C}_2\text{H}_5\text{NH}_2 \rightarrow \text{Si(\text{NH}_2\text{C}_6\text{H}_5)_4} + 4\text{C}_2\text{H}_5\text{NH}_2\cdot\text{HCl}$$

Tetraethylaminosilane is a colorless oil, which does not freeze at low temperatures, is soluble in most organic solvents, and keeps for a long time in the absence of moisture. Like all compounds of this series, it is easily decomposed by water, forming hydroxysilanes. Tetraphenylaminosilane, Si(NHC$_6$H$_5$)$_4$, was prepared (as long ago as 1888) by reacting SiCl$_4$ and aniline in benzene solution (Bibl.16).

Other representatives of this series have also been prepared (Bibl.26).

\begin{align*}
\text{Si(\text{a-NHC}_6\text{H}_5\text{CH}_3)_4} & \quad \text{Si(\text{a-NHC}_6\text{H}_5\text{H})_4} \\
\text{Si(\text{a-NHC}_6\text{H}_5\text{CH}_3)_4} & \quad \text{Si(\text{a-NHC}_6\text{H}_5\text{H})_4}
\end{align*}

These compounds are stable on heating up to 200$^\circ$C, crystallise readily, easily dissolve in benzene, have constant melting points, and exist in the monomeric form.

Tetraphenylaminosilane has been investigated in more detail. Under the action of HCl, its cleavage occurs, forming SiCl$_4$:

$$\text{Si(\text{NH}_2\text{C}_6\text{H}_5)_4} + 4\text{HCl} \rightarrow \text{SiCl}_4 + 4\text{C}_6\text{H}_5\text{NH}_2$$

This reaction is common to the aminosilanes.

The action of HCl on the aminosilanes may be compared to that of acetyl chloride, benzoyl chloride, or POCl$_3$ on the ethyl ester of orthosilicic acid:

$$\text{Si(OR)}_4 + 4\text{CH}_2\text{COCI} \rightarrow \text{SiCl}_4 + 4\text{CH}_2\text{COOR}$$
The reaction of tetraphenylamnosilane with bromine in benzene solution leads to the formation of a compound of the composition $\text{Si[NC}_6\text{H}_3\text{Br}_2]_2$, accompanied by strong heating of the mixture (Bibl.26). The reaction takes place in three stages. In the first stage, 2 atoms of bromine cause cleavage of one aniline molecule. The reaction product is a very viscous liquid, which does not crystallize even at a low temperature. The reaction follows the formula:

\[
\text{Si(NHC}_6\text{H}_4)_4 + \text{Br}_2 \rightarrow \text{Si(NC}_6\text{H}_4\text{Br})_2 + \text{C}_6\text{H}_6\text{NH}_4\cdot\text{HBr}
\] (1)

In the second stage, di-(phenylamino)-p-bromophenyliminosilane reacts with more bromine, splitting off still another aniline molecule and forming di-(bromophenylimino)silane.

\[
\text{Si(NC}_6\text{H}_4\text{Br})_2 + \text{Br}_2 \rightarrow \text{Si(NC}_6\text{H}_4\text{Br})_2 + \text{C}_6\text{H}_6\text{NH}_4\cdot\text{HBr}
\] (2)

In the third stage, under the action of a third molecule of bromine, a third molecule of aniline is split off, forming p-dibromophenylnitrylsilane.

\[
\text{Si(NC}_6\text{H}_4\text{Br})_2 + \text{Br}_2 \rightarrow \text{Si(C}_6\text{H}_4\text{Br})_2 + \text{C}_6\text{H}_6\text{NH}_4\cdot\text{HBr}
\] (3)

The substance so obtained has a dark brown color, softens gradually on heating, and becomes completely liquid at 60°C. It is soluble in benzene, and readily reacts with water even in benzene solutions.

The third and final stage of the reaction between bromine and tetraphenylamnosilane is regulated by diluting the reaction mixture with benzene, or by adjusting the quantity of bromine taken for the reaction.

Together with these compounds, products of the substitution of bromine atoms for hydrogen atoms of the phenyl groups are also formed in the solutions, liberating HBr.
The formation of a more highly brominated compound of the type

$$\text{Br}_2\text{C}_6\text{H}_5\text{N} = \text{Si} = \text{NC}_6\text{H}_5\text{Br}_2$$

is also possible. The prolonged action of bromine leads to the formation of SiBr₄, HBr, and a mixture of tribromoaniline with still more highly brominated anilines.

Another representative of the tetraaminosilanes series, tetraethylphenylaminosilane, has been prepared by reacting SiCl₄ with ethylaniline. The principal reaction product is ethylaniline hydrochloride, tetraethylphenylaminosilane being formed only in small quantities (Bibl.27).

The reaction may be represented as follows:

$$\text{SiCl}_4 + 8\text{HN}<\text{C}_6\text{H}_5\text{Si}<\text{C}_6\text{H}_5\text{Si} \longrightarrow \text{Si}(\text{N}<\text{C}_6\text{H}_5\text{Si})_4 + \text{C}_6\text{H}_5\text{SiCl}_3$$

The reaction of diethylaniline with SiCl₄ yields ethylaniline hydrochloride and an oily product corresponding in composition to tetra-(ethylphenylamino)silane (Bibl. 28).

A reversible reaction takes place between methyltrichlorosilane and aniline to form aniline hydrochloride and methyltriphenylaminosilane. Ethyltrichlorosilane and diphenyl dichlorosilane react similarly.

The exchange reactions between alkylarylaminosilanes and halosilanes have been studied (Bibl.29), which follow the pattern:

$$4(\text{CH}_3\text{SiNHH}_3) + \text{SiBr}_3 \rightarrow 4(\text{CH}_3\text{SiBr}) + \text{Si(NHH}_3\text{Si})_3$$

Aminosilanes react very readily with acids, breaking the Si – N bond. Thus, from 7 g of CH₃Si(NH₂C₆H₅)₃ in benzene, under the action of an excess of dry HBr, 3.5 g of CH₃SiBr₃ is formed.
Sulfuric acid reacts, producing strong heating, with \((\text{C}_2\text{H}_5)_3\text{SiNHCH}_3\), forming aniline sulfate and a solution of \((\text{C}_2\text{H}_5)_3\text{Si} - 0 - \text{SO}_2 - 0 - \text{Si}(\text{C}_2\text{H}_5)_3\), hexaethyldioxysulfoxonodisilane.

The dialkyldiphenylaminosilanes do not react with \(\text{CCl}_4\), benzyl chloride, stannous bromide, nor mercurous chloride.

Diphenylalanine and diphenylamine do not react with \(\text{SiCl}_4\). The nature of the radicals replacing hydrogen in the amine molecule affects this reaction.

**Physical Properties of Aminosilanes and Alkyl-(aryl)-aminosilanes**

The aminosilanes and the alkyl-(aryl)-aminosilanes distil without decomposition. They are readily soluble in hydrocarbons, halogen derivatives of the hydrocarbons, ethers, and mixtures of these solvents. They are readily hydrolyzed under the action of water or water vapor. This is especially true of the lower representatives of this class of compounds.

Table 69 gives the physical properties of the aminosilanes and alkyl-(aryl)-aminosilanes.

**Conversion of Alkyl-(aryl)-aminosilanes into Polymers**

The detailed study of the polymeric organoaminosilanes began at a relatively recent date. As already noted, under the action of ammonia (taken in excess) on monochlorosilane, gaseous products are at first formed, and then condense into nonvolatile, viscous, and even solid polymeric compounds of the following structure:

Polymeric nitrogen-containing compounds display a certain structural similarity with the polysiloxanes. The conversion of the primary compound \(\text{SiH}_3\text{NH}_2\), which is easily formed, into \((\text{SiH}_3)_2\text{NH}\) resembles the reactions of hydrolysis of \(\text{SiH}_2\text{Cl}\) and the conversion of that compound into \((\text{SiH}_3)_2\text{O}\). The compounds \(\text{SiH}_3\text{NH}_2\) and \((\text{SiH}_3)_2\text{NH}\) are
<table>
<thead>
<tr>
<th>a) Name</th>
<th>b) Formula</th>
<th>c) °C</th>
<th>d) °C</th>
<th>e)</th>
<th>f)</th>
<th>g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aminotrisilane</td>
<td>((\text{H}_2\text{Si})_3\text{N})</td>
<td>-105.6</td>
<td>52.0</td>
<td>0.895 (at -106°)</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>Tri-(ethyl)-aminasilane</td>
<td>((\text{C}_3\text{H}_7\text{Si})_2\text{SiNH}_2)</td>
<td>134</td>
<td>136.8-137.8</td>
<td>-</td>
<td>1,4259-1,4260</td>
<td>13</td>
</tr>
<tr>
<td>Methylaminodisilane</td>
<td>((\text{H}_2\text{Si})_2\text{NCH}_3)</td>
<td>32.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>18</td>
</tr>
<tr>
<td>Ethylaminodisilane</td>
<td>((\text{H}_2\text{Si})_2\text{NCH}_3)</td>
<td>65.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>18</td>
</tr>
<tr>
<td>Tri-(pyrrol)-silane</td>
<td>(\text{HSi(C}_4\text{H}_4\text{N})_2)</td>
<td>210 (50 mm) breaks down</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>15,16</td>
</tr>
<tr>
<td>Tri-(phenyl)-aminasilane</td>
<td>((\text{C}<em>6\text{H}</em>{5})_2\text{SiNH}_2)</td>
<td>55-56</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>16</td>
</tr>
<tr>
<td>Tri-(phenylaminosilane)</td>
<td>(\text{HSi(NHC}_4\text{H}_4\text{H})_3)</td>
<td>114 (b.d.)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>15,16</td>
</tr>
<tr>
<td>Hexamethyl-(methylamino)-</td>
<td>(\text{[(CH}_3\text{Si)}_2\text{NCH}_3)</td>
<td>-</td>
<td>143.0-147.0</td>
<td>-</td>
<td>-</td>
<td>44</td>
</tr>
<tr>
<td>disilane</td>
<td>((\text{CH}_3\text{Si})_2\text{SiNHCH}_3)</td>
<td>70.0 (747 mm)</td>
<td>0.7395</td>
<td>1,3905</td>
<td>-</td>
<td>13</td>
</tr>
<tr>
<td>Tris(trimethylamino)-</td>
<td>((\text{CH}_3\text{Si})_2\text{SiNCH}_3)</td>
<td>90.1-90.8</td>
<td>-</td>
<td>-</td>
<td>1,3912</td>
<td>13</td>
</tr>
<tr>
<td>silane</td>
<td>((\text{CH}_3\text{Si})_2\text{Si(C}_4\text{H}_7\text{H})_2)</td>
<td>126.1-126.4 (750 mm)</td>
<td>-</td>
<td>-</td>
<td>1,4112</td>
<td>13,24</td>
</tr>
<tr>
<td>Trimethyl-(diethylamino)-</td>
<td>((\text{CH}_3\text{Si})_2\text{Si[N(CH}_3\text{)]_2})</td>
<td>-</td>
<td>125.4-125.6</td>
<td>0.7742 (vacuum)</td>
<td>1,4080</td>
<td>14</td>
</tr>
<tr>
<td>silane</td>
<td>((\text{CH}_3\text{Si})_2\text{Si(NHC}_4\text{H}_4\text{H})_3)</td>
<td>-</td>
<td>206</td>
<td>-</td>
<td>-</td>
<td>29</td>
</tr>
<tr>
<td>Dimethyl-(phenylamino)-</td>
<td>((\text{CH}_3\text{Si})_2\text{Si(NHC}_4\text{H}_4\text{H})_2)</td>
<td>-</td>
<td>98-99 (19 mm)</td>
<td>-</td>
<td>-</td>
<td>29</td>
</tr>
<tr>
<td>silane</td>
<td>((\text{CH}_3\text{Si})_2\text{Si(NHC}_4\text{H}_4\text{H})_3)</td>
<td>-</td>
<td>185-186 (9 mm)</td>
<td>-</td>
<td>-</td>
<td>29</td>
</tr>
<tr>
<td>Methyltri-(phenylamino)-</td>
<td>((\text{CH}_3\text{Si})_2\text{Si(NHC}_4\text{H}_4\text{H})_3)</td>
<td>-</td>
<td>345</td>
<td>-</td>
<td>-</td>
<td>29</td>
</tr>
<tr>
<td>silane</td>
<td>((\text{C}<em>6\text{H}</em>{5})_3\text{Si(NHC}_4\text{H}_4\text{H})_2)</td>
<td>-</td>
<td>212 (1 mm)</td>
<td>-</td>
<td>-</td>
<td>29</td>
</tr>
<tr>
<td>Triethyl-(phenylamino)-</td>
<td>((\text{C}<em>6\text{H}</em>{5})_3\text{Si(NHC}_4\text{H}_4\text{H})_2)</td>
<td>-</td>
<td>270</td>
<td>-</td>
<td>-</td>
<td>29</td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Melting point; d) Boiling point; e) Specific gravity; f) Refractive index; g) Bibliography
<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c)</th>
<th>d)</th>
<th>e)</th>
<th>f)</th>
<th>g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethyl-diphénylamino-silane</td>
<td>(C₆H₅Si(HNC₆H₅)₂)</td>
<td>181–181</td>
<td>350</td>
<td>172–173 (1 mm)</td>
<td>-</td>
<td>73</td>
</tr>
<tr>
<td>Ethyltri-diphénylamino-silane</td>
<td>(C₆H₅)Si(HNC₆H₅)₃</td>
<td>-</td>
<td>381</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Diphenyldi-diphénylamino-silane</td>
<td>(C₆H₅)₂Si(HNC₆H₅)₂</td>
<td>-</td>
<td>232–234 (1 mm)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Tetramethyl-diphénylamino-silane</td>
<td>[(C₆H₅)₄Si]₂NH</td>
<td>175</td>
<td>413</td>
<td>0.8079</td>
<td>14.22, 23</td>
<td></td>
</tr>
<tr>
<td>Hexaethylaminodisilane</td>
<td>[[(C₆H₅)₆Si]₂NH]</td>
<td>dist. at (1 mm)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Triphenyl-diphénylamino-silane</td>
<td>(C₆H₅)₂Si(NHC₆H₅)₂</td>
<td>45</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hexaphenylaminodisilane</td>
<td>[(C₆H₅)₃Si]₃NH</td>
<td>175</td>
<td>-</td>
<td>crystals stable in air</td>
<td>-</td>
<td>19</td>
</tr>
<tr>
<td>Octamethylaminotrisilane</td>
<td>[[(C₆H₅)₅Si]₂NH₂Si(CH₃)₂]</td>
<td>-</td>
<td>192–196 (756 mm)</td>
<td>0.8366</td>
<td>1.4281</td>
<td>31</td>
</tr>
<tr>
<td>Tetra-(ethylamino)-silane</td>
<td>(C₆H₅NH)₄Si</td>
<td>-</td>
<td>102 (20 mm)</td>
<td>-</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>Tetrapyrrrolsilane</td>
<td>(C₆H₅NH)₄Si</td>
<td>173.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>43</td>
</tr>
<tr>
<td>Tetra-(p-tolylamino)-silane</td>
<td>(C₆H₅NH₂)(C₆H₅)₂Si</td>
<td>136–137</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>16.26</td>
</tr>
<tr>
<td>Tetra-(o-tolylamino)-silane</td>
<td>(C₆H₅NH₂)(C₆H₅)₂Si</td>
<td>131–132</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>16.26</td>
</tr>
<tr>
<td>Tetrap-(α-naphthylamino)-silane</td>
<td>(C₆H₅NH)(C₆H₅)₂Si</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>16.26</td>
</tr>
<tr>
<td>Tetrap-(β-naphthylamino)-silane</td>
<td>(C₆H₅NH)(C₆H₅)₂Si</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>16.26</td>
</tr>
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</table>
highly volatile. Nitrogen-containing compounds of this type, like the hydroxysilanes, tend to form polymers. Cyclic polymers \( (\text{R}_2\text{SiH})_n \) and linear polymers of the type \( n \text{R}_2\text{SiHN} \text{SiR}_3 \) have recently been isolated and studied (Bibl.30).

The products of the reaction between methyl- and ethylchlorosilanes and ammonia are mainly hexamethyl- (hexaethyl)-cyclotriaminosilanes and octamethyl- (octaethyl)-cyclotetraaminosilanes, together with a number of other mixed cyclic polymers (Bibl.31).

**Preparation of Hexamethylcyclotriaminosilane and Octamethylcyclotetraamino-
silane.** In a 5-liter three-neck flask, provided with a stirrer, condenser, and gas induction tube, 903 g of dimethylchlorosilane dissolve in 3.5 liters of dry benzene is placed. Dry ammonia is passed through the gas tube onto the surface of the liquid, and on vigorous stirring is absorbed by it. During the reaction the temperature is held below 30°C. After 4 hours, the \( \text{M}_4\text{Cl} \) being precipitated begins to impede the stirring of the mixture. To facilitate the separation of the liquid from the deposit of \( \text{M}_4\text{Cl} \), the mixture is heated, and the precipitate takes a finely crystalline form and can be easily filtered off. After filtration the mixture is treated with ammonia for 2 hours more. The additional ammonium chlorides thrown down is then filtered off, and the benzene is distilled off, giving 115 g (81%) of a crude mixture of aminosilanes. The mixture is fractionally distilled, giving 185 g of hexamethylcyclotriaminosilane and 210 g of octamethylcyclotetraaminosilane. The latter is purified by recrystallization from petroleum ether. The undistilled residue amounts to 20 g.

**Preparation of Hexamethylcyclotriaminosilane without a Solvent** (Bibl.30). In a round-bottomed flask, provided with a reflux condenser, a stirrer, and a dropping funnel with its end drawn out into a capillary tube, 500 ml of liquid ammonia is placed, and 140 g of dimethyl dichlorosilane (1.06 mol) is added gradually to it from the funnel. The flask and the condenser are cooled by a mixture of solid carbon dioxide and acetone. After adding the dimethyl dichlorosilane, the stirring is continued for 15 min. The mixture is then extracted with 250 ml of benzene. The precipi-
tate of ammonium chloride remaining in the flask is washed four times with small portions of benzene, all the benzene extracts are combined, and the benzene is distilled off. After this has been done, the residue weighs 60 g. Its fractionation yields 33 g of hexamethylocyclotriaminosilane.

**Preparation of Polydiethylocycloaminosilanes.** In a 400 ml flask 300 ml of absolute ether is placed, and is made up with ammonia to a total volume of 400 ml; 515 g of a mixture of diethyldichlorosilane and diethydimethylchlorosilane, taken in molecular proportions, is now diluted with 1200 ml of absolute ether; this mixture is added in three equal portions to the solution of ammonia in ether. The mixture is allowed to stand 15 min., and the ammonium chloride is then filtered off. It is washed several times with ether, and the ethereal extracts are combined with the filtrate, after which the ether is distilled off from the reaction product. Simple distillation of the product gives 143 g of a distillate boiling below 235°C. The individual products cannot be separated by simple distillation. Fractionation of the residue under reduced pressure yields 24 g of a product with a wide boiling range, probably consisting of tetraethyldimethylaminodisilane and octaethylcyclohexaminosilane (41 g). The distillation residue amounts to about 20 g.

To obtain a better yield of aminosilane, 157 g of diethyldichlorosilane dissolved in 1000 ml of ether is placed in a flask and saturated with ammonia (without external cooling). The saturation is continued until the contents of the flask begin to freeze as a result of the vigorous boiling of the excess of liquid ammonia. The separation of the ammonium chloride is considerably more difficult, in this case, owing to its exceptionally fine grain. It is entirely impossible to separate it completely from the products of the reaction, and it sublimes during the distillation, contaminating the aminosilanes. The 54 g of reaction products yields 14.6 g of hexaethylcyclohexaminosilane. The slightly lowered nitrogen content of the trimer gives grounds for supposing it to be contaminated by compounds of linear structure, of the type

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Preparation of Diethyltetramethylaminodisilane. In twice its volume of ether, 284 g of ethyldimethylchlorosilane, obtained by reacting dimethyldichlorosilane with ethylmagnesium bromide, is dissolved. The solution is added to an ethereal solution of ammonia, according to the method we have described for the preparation of poly-di-ethylcycloaminosilanes. Most of the ether is distilled off from the reaction product. The product, boiling above 45°C, is fractionated. After the remaining traces of ether are distilled off, the temperature falls to 23°C, and then rises again; at first to 95°C, and then, rapidly, from 104°C to 157°C, giving off a considerable quantity of ammonia. The fractionation yields 26 g of ethyldimethylaminosilane and 33 g of s-tetramethyltetramethylaminodisilane. The residue of 33 g consists mainly of diethyltetramethylaminodisilane. The fall in the temperature was due to the liberation of ammonia owing to the dearination of ethyldimethylaminosilane:

\[ 2 \text{CH}_3\text{N(SiH}_2\text{CH}_3\text{)} \rightarrow \text{CH}_3\text{N(SiH}_2\text{CH}_3\text{)} + \text{NH}_3 \]

Ethyldimethylaminosilane, probably, is formed at room temperature and is stable under these conditions, but is decomposed on heating to below the boiling point.

Preparation of Octamethylaninotrisilane. A mixture of 81 g of hexamethylaninoisilane, 37 g of hexamethylocyclotraminosilane, and 0.5 g of ammonium chloride, is heated in an 130 ml bomb at 300 - 325°C for 26 hours. The pressure in the bomb rises from 175 kPa to 213 kPa. When the bomb is opened, a considerable amount of ammonia is given off. The reaction product is fractionated in a column with 15 theoretical plates, yielding 60 g of hexamethylaminodisilane and 19 g of octamethylaninotrisilane.

The thermal rearrangement reaction also proceeds at 450°C in 14 hours, and at 350°C in 2 hours. In all cases the rectification curves coincide, which is evidence that equilibrium is established in the process of thermal rearrangement.
Preparation of Trimethylcyclotriarinosilane. In the same way described for the preparation of polyethylocyclopolyarinosilanes, 230 g of methyl dichlorosilane is treated with ammonia. After the ether has been distilled off, 60 g of a viscous oily substance is obtained, which does not boil when heated to 195°C. This oily product is subjected to thermal rearrangement in a stream of nitrogen, yielding 25 g of a mobile liquid. Ammonia is given off during the process of degradation. The residue in the flask is a porous, brittle resin, which shows no change on further heating, and reacts very slowly with an alcoholic solution of KOH.

When the collected distillate is fractionated, it gradually decomposes, evolving ammonia.

After 5.2 ml of a fraction boiling from 166 - 169°C has been collected, the contents of the flask coagulate. The gel reacts with considerably more energy with an alcoholic solution of alkali than the residue after thermal rearrangement did.

To judge by its boiling point, the distillate is an impure trimethylcyclotriarinosilane.

The evolution of ammonia during the thermal degradation, as well as during distillation, is evidence of the following rearrangement:

\[
\begin{align*}
\text{H}_3\text{SiNH}_3 + \text{H}_2\text{Si} &\rightarrow [\text{H}_3\text{Si}]_n + \text{NH}_3
\end{align*}
\]

The tendency to form cyclical compounds is more pronounced in the amino derivatives than in the siloxanes. The yield of cyclic trimer is 45 - 55% in the case of the aminosilane, and 0.5% in that of the siloxane.

Table 70 gives the physical properties of cyclic polyalkylaminosilanes.

Alkoxy-(aryloxy)-Aminosilanes

The alkoxyaminosilanes may be regarded as amides of orthosilicic acid, and arranged in the following series:

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Like the amides of the carboxylic acids, they enter into the reactions of hydrolysis, alcoholysis, and aminolysis.

Table 70

Physical Properties of Cyclic Polyalkylaminosilanes (Bibl. 30, 31)

<table>
<thead>
<tr>
<th>a) Name</th>
<th>b) Formula</th>
<th>c) Boiling point °C</th>
<th>d) Melting point °C</th>
<th>e) Refractive index $n^2_0$</th>
<th>f) Specific gravity, $d^2_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexamethyldicyclosilane</td>
<td>$[(\text{CH}_3)_2\text{SiNH}]_3$</td>
<td>138</td>
<td>-10</td>
<td>1.4448</td>
<td>0.9198</td>
</tr>
<tr>
<td>Octamethyldicyclosilane</td>
<td>$[(\text{CH}_3)_2\text{SiNH}]_4$</td>
<td>255</td>
<td>97</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hexamethylcyclotri-(aminosilane)</td>
<td>$[(\text{CH}_3)_2\text{SiNH}]_3$</td>
<td>150</td>
<td>-41</td>
<td>1.4670</td>
<td>0.9287</td>
</tr>
<tr>
<td>Octamethylcyclotetra-(aminosilane)</td>
<td>$[(\text{CH}_3)_2\text{SiNH}]_4$</td>
<td>190-192</td>
<td>16</td>
<td>1.4769</td>
<td>0.9521</td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Boiling point °C; d) Melting point °C; e) Refractive index $n^2_0$; f) Specific gravity, $d^2_4$

The tert-alkoxyaminosilanes have acquired the greatest practical importance. These are compounds in which at least one tertiary alkoxy group and one amino group are attached to one silicon atom.

They may be prepared in two stages from $\text{SiCl}_4$, the corresponding alcohol, and ammonia. If all the alkoxy groups are required to be tertiary, the reaction between the tertiary alcohol and $\text{SiCl}_4$ is conducted in the presence of an acceptor of acid, for example pyridine.

In the first stage of the synthesis, the tert-alkoxychlorosilane is obtained. Treatment with ammonia then converts it into the corresponding aminosilane:

$$2\text{ROH} + \text{SiCl}_4 + 2\text{C}_2\text{H}_5\text{N} \rightarrow (\text{RO})_2\text{SiCl}_3 + 2\text{C}_2\text{H}_5\text{N.HCl}$$

$$\text{(RO)}_2\text{SiCl}_3 + 4\text{NH}_3 \rightarrow (\text{RO})_2\text{Si(\text{NH}_3})_2 + 2\text{NH}_4\text{Cl}$$
By appropriate choice of the starting materials and the reaction conditions, mono-, di- and tri-tert-alkoxyaminoalkylsilanes may be prepared. Tert-alkoxytrichlorosilane reacts first with ammonia, forming soluble and fusible resinous condensation products, which continue to undergo condensation, liberating ammonia, and soon become insoluble and infusible. Trialkoxymonochlorosilane and dialkoxydichlorosilane, on the contrary, do not form the corresponding aminosilanes in good yield.

On treatment of di-tert-butoxydichlorosilane with ammonia, di-tert-butoxydiaminoalkylsilane, \((\text{C}_4\text{H}_9\text{O})_2\text{Si}(\text{NH}_2)_2\), is formed. Alkoxyalkylsilanes of the type \((\text{RO})_x(\text{R}''\text{O})_y\text{Si}(\text{NH}_2)_2\) have been synthesized by this method, \(R\) and \(R''\) varying from \(\text{CH}_3\) to \(\text{C}_4\text{H}_9\) and \(x+y\) from 2 to 3.

Table 71 gives the properties of certain tert-alkoxyaminoalkylsilanes.

The most important representative of this series of compounds is di-tert-butoxydiaminoalkylsilane. On hydrolysis of this compound by cold water, di-tert-butoxydiol is formed. It is readily resinified on heating or during the very process of hydrolysis at an elevated temperature.

When alcohols act on dibutoxydiaminoalkylsilane, the liberation of ammonia and the formation of dibutoxydi-alkoxyalkylsilanes are observed. Methanol reacts rapidly, while the other alcohols replace only one amino group. For complete substitution, heating is necessary. The tertiary alcohols react very slowly.

The amino groups in di-tert-butoxydiaminoalkylsilane may also be replaced by the

\[ R - NH - \text{group, or by the acid residue } R - COO - \]

\[ \text{CH}_3\text{CO}_2\text{Si}(\text{NH}_2)_2 + 2\text{RNH}_2 \rightarrow \text{CH}_3\text{CO}_2\text{Si}(\text{NH})_2\text{R} + 2\text{NH}_2 \]

\[ \text{CH}_3\text{CO}_2\text{Si}(\text{NH}_2)_2 + 4\text{RCOOH} \rightarrow \text{CH}_3\text{CO}_2\text{Si}(\text{OCOR})_2 + 2\text{RCOONH}_2 \]

When tert-butoxytrichlorosilane is treated with ammonia, polymeric products are obtained.

On heating to 200°C, dibutoxydiaminoalkylsilane gives off ammonia and forms a cyclic polymer of the composition \([(\text{C}_4\text{H}_9\text{O})_2\text{SiNH}]_x\).
Table 71
Physical Properties of Alkoxyaminosilanes (Bibl.32)

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c) °C</th>
<th>d) d&lt;sub&gt;4&lt;/sub&gt;</th>
<th>e) n&lt;sub&gt;D&lt;/sub&gt;</th>
</tr>
</thead>
</table>
| Methoxy-tert-butoxydi-
aminosilane | (CH<sub>3</sub>)<sub>2</sub>CO<sub>2</sub>Si(NH<sub>2</sub>)<sub>2</sub> | 62-65 | 1.4130            |                  |
| Ethoxy-tert-butoxydi-
aminosilane  | (CH<sub>3</sub>)<sub>2</sub>CHO<sub>2</sub>Si(NH<sub>2</sub>)<sub>2</sub> | 63-66 | 1.4185            |                  |
| Isopropanoxy-tert-butoxydi-
aminosilane | (CH<sub>3</sub>)<sub>2</sub>CHO<sub>2</sub>Si(NH<sub>2</sub>)<sub>2</sub> | 64-65 | 1.4170            |                  |
| Butoxy-tert-butoxydi-
aminosilane  | (CH<sub>3</sub>)<sub>2</sub>CHO<sub>2</sub>Si(NH<sub>2</sub>)<sub>2</sub> | 66-68 | 1.4280            |                  |
| Sec-butoxy-tert-butoxydi-
aminosilane | (CH<sub>3</sub>)<sub>2</sub>CHO<sub>2</sub>Si(NH<sub>2</sub>)<sub>2</sub> | 92-95 | 1.4210            |                  |
| Di-tert-butoxydi-
aminosilane   | (CH<sub>3</sub>)<sub>2</sub>CHO<sub>2</sub>Si(NH<sub>2</sub>)<sub>2</sub> | 70-72 | 1.4292            |                  |
| Di-tert-propoxydi-
aminosilane    | (CH<sub>3</sub>)<sub>2</sub>CHO<sub>2</sub>Si(NH<sub>2</sub>)<sub>2</sub> | 105-110 | 1.4390         |                  |
| Tri-tert-butoxy-
aminosilane     | (CH<sub>3</sub>)<sub>2</sub>CHO<sub>2</sub>Si(NH<sub>2</sub>)<sub>2</sub> | 82-85 | 1.4080            |                  |
| Methoxy-tert-butoxydi-
aminosilane | (CH<sub>3</sub>)<sub>2</sub>CO<sub>2</sub>Si(NH<sub>2</sub>)<sub>2</sub> | 72-73 | 1.4052            |                  |
| Butoxydi-tert-butoxy-
aminosilane | (CH<sub>3</sub>)<sub>2</sub>CO<sub>2</sub>Si(NH<sub>2</sub>)<sub>2</sub> | 113-114 | 1.4149         |                  |
| Isopropanoxy-tert-butoxydi-
aminosilane | (CH<sub>3</sub>)<sub>2</sub>CHO<sub>2</sub>Si(NH<sub>2</sub>)<sub>2</sub> | 83-84 | 1.4050            |                  |
| Diisopropanoxy-tert-
butoxyaminosilane | (CH<sub>3</sub>)<sub>2</sub>CHO<sub>2</sub>Si(NH<sub>2</sub>)<sub>2</sub> | 57-60 | 1.4015            |                  |

**a)** Name; **b)** Formula; **c)** Boiling point; **d)** Specific gravity; **e)** Refractive index
The butoxyaminosilanes are used to prepare water-repellant films on materials that could react with HCl, and which could consequently not be made water-repellant by treatment with vapors of alkylchlorosilanes.

The reaction of di-tert-butoxyaminosilane with amino-alcohols forms esters of orthosilicic acid containing an amino group in the organic radical (Bibl.31).

\[ \text{(C}_4\text{H}_6\text{O})_3\text{Si(NH}_2\text{)}_2 + 2\text{HOCH}_2\text{CH}_2\text{NH}_2 \rightarrow (\text{C}_4\text{H}_6\text{O})_3\text{Si(OCH}_3\text{CH}_2\text{NH}_2\text{)}_2 + 2\text{NH}_3 \]

The reaction proceeds for several hours on boiling an equimolecular mixture of the reagents. Its course is followed by determining the loss of weight due to the ammonia evolved. On conclusion of the reaction, the mixture is fractionated under reduced pressure.

The products so synthesized are viscous, colorless liquids with a faint odor. Products 1 and 6 (cf. Table 72) are soluble in water. Product 1 is soluble in ligroin, benzene, CCl₄, alcohol, acetone, ether, and pyridine. Most of the products are basic in character, and are titrated quantitatively against HCl, using methyl red as an indicator. In some cases, side reactions leading to the formation of butanol and hexabutoxyaminodisilane

\[ (\text{C}_4\text{H}_6\text{O})_3\text{SiNH}_2\text{Si(OCH}_3\text{H}_4\text{)}_2 \]

are observed in the course of the synthesis.

During the synthesis of product 2, a fraction (Bibl.12) was separated, with boiling point 130°C, refractive index nD²⁰ = 1.4261, and specific gravity d₂⁰ = 0.9181, consisting of dibutoxy-(2-diethylaminoethoxy)-aminosilane;

\[ (\text{C}_4\text{H}_6\text{O})_3[(\text{C}_4\text{H}_6)]_3\text{NCH}_2\text{CH}_2\text{O}]\text{SiNH}_2 \]

Preparation of Di-tert-butoxydi-(aminoethoxy)-aminosilane. A solution of 1 mol of di-tert-butoxydiaminopolane and 2 mols of aminoethyl alcohol is heated 1 to 3 hours at 150 - 200°C. After the theoretical quantity of hydrogen has been evolved,
the product is distilled under reduced pressure, giving di-tert-butoxy(di-
aminooxy)silane in yields ranging from 40 to 70% of theoretical (Bibl.31).

By using different amino-alcohols, a number of tert-butoxyaminopolysiloxanes
are prepared. Their properties are given in Table 72.

Table 72
Physical Properties of Di-tert-butoxyaminoalkysilanes

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c)</th>
<th>d)</th>
<th>e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name;</td>
<td>Formula;</td>
<td>Boiling point, °C;</td>
<td>Refractive index,</td>
<td>Specific gravity,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>d20</td>
<td>nD</td>
<td></td>
</tr>
<tr>
<td>Di-tert-butoxy-di(aminooxy)-silane</td>
<td>[CH3]3CO2Si(OCH2CH2NH2)2</td>
<td>144</td>
<td>1.4269</td>
<td>0.9731</td>
</tr>
<tr>
<td>Di-tert-butoxy-di(diethylaminooxy)-silane</td>
<td>[CH3]3CO2Si(OCH2CH2CH2NH2)2</td>
<td>197</td>
<td>1.4272</td>
<td>0.9090</td>
</tr>
<tr>
<td>Di-tert-butoxy-di(aminopropoxy)-silane</td>
<td>[CH3]3CO2Si(OCH2CH2CH2NH2)2</td>
<td>107</td>
<td>1.4264</td>
<td>0.9548</td>
</tr>
<tr>
<td>Di-tert-butoxy-di(diethoxypropoxy)-silane</td>
<td>[CH3]3CO2Si(OCH2CH2CH2CH2NH2)2</td>
<td>133</td>
<td>1.4266</td>
<td>0.9462</td>
</tr>
<tr>
<td>Di-tert-butoxy-di(aminomethyl-3-propoxy)-silane</td>
<td>[CH3]3CO2Si(OCH2CH2CH2NH2CH2CH2CH2NH2)2</td>
<td>126</td>
<td>1.4246</td>
<td>0.9324</td>
</tr>
<tr>
<td>Di-tert-butoxy-di(aminomethyl-6-butoxy)-silane</td>
<td>[CH3]3CO2Si(OCH2CH2CH2CH2NH2CH2CH2CH2NH2)2</td>
<td>187</td>
<td>1.4495</td>
<td>0.9911</td>
</tr>
</tbody>
</table>

Hydrolysis of Alkoxysilanes

The tertiary alkoxysilanes are readily hydrolyzed with liberation of am-
monia, forming the corresponding alkoxysilanols

\[ (RO)3Si(NH)2 + 2H2O \rightarrow (RO)3Si(OH)2 + 2NH3 \]

It should be noted that the stability of the tertiary alkoxy groups to hydroly-
sis, especially in an alkaline medium, is characteristic for the tertiary alkoxy-
silanes and tertiary polyalkoxysiloxanes.
The tertiary alkoxy polysiloxane resins may remain in contact with water (vapor or liquid) for a long time without visible change in their properties.

The stability of such resins, prepared from the corresponding tertiary alkoxyamino silanes, to hydrolysis, and their hydrophobic character, are utilized in practice.

Hydrolysis of Di-tert-butoxyaminosilane. A mixture of 9.5 g of di-tert-butoxyaminosilane and 20 g of ground ice is shaken for 5 min. White needles are thrown down from the reaction mixture, and are dissolved in 100 g of low-boiling petroleum ether. The ether layer is separated and evaporated under reduced pressure, yielding 5.37 g of white needles, melting at 99 - 101°C, which, according to the analytical results, correspond to di-tert-butoxysilanediol. The water layer is separated and extracted twice with 50 cm³ portions of ether. The ether extracts are dried over anhydrous potassium carbonate for 1 hour, and are then filtered and evaporated under reduced pressure. The residue (3.75 g) consists of crystals of di-tert-butoxysilanediol and products of its condensation.

According to the degree of condensation, high-viscosity liquids, soluble or insoluble resins, or hard infusible products may be obtained.

Reactions of Alcoholysis and Aminolysis of Alkoxyaminosilanes

The dialkoxyaminosilanes react readily with most primary and secondary alcohols at ordinary temperatures to form mixed ortho-esters:

\[(RO)_2Si(NH)\_2 + 2R'OH \rightarrow (RO)\_3Si + 2NH\_3\]

Both amino groups readily enter into the reaction with methanol. The higher alcohols, however, react with the second amino group only on heating.

At an elevated temperature the second amino group reacts more readily with primary alcohols than with secondary. With tertiary alcohols the reaction proceeds very slowly, and the second amino group does not participate in the reaction at all.
It must be noted that the di-tert-alkoxydichlorosilanes display higher activity toward alcohols than the corresponding aminosilanes do. In the case of the chlorosilanes, the reaction is conducted in the presence of tertiary amines, for instance pyridine.

Polyhydric alcohols react with alkoxysilanes to form various products: liquids of various degrees of viscosity, insoluble and infusible gels and powders.

Alkyd resins, which regarded as a special class of derivatives of polyhydric alcohols, react very readily with di-tert-alkoxyaminosilanes. The admixture of small quantities of alkoxysilanes with the alkyd resins improves certain of their properties, and may be used to accelerate their gelation. Complete alcoholysis of alkoxysilanes or alkoxychlorosilanes leads to the formation of mixed orthoesters distinguished by their resistance to hydrolysis. The introduction of even a single tertiary alkoxy group into the ortho-esters considerably increases their resistance to water, since such alkoxy groups exert a stabilizing influence on the primary alkoxy groups attached to the same silicon atom (Bibl.32).

When heated to 200°C, the di-tert-alkoxydiaminosilanes, which under ordinary conditions are stable compounds, undergo intramolecular condensation to form polyalkoxyaminoalkoxycycloaminosilanes:

\[ x(RO)_{2}Si(NH)_{2} \xrightarrow{\text{catalyst, heating}} [(RO)_{2}SiNH]_{x} + xNH_{3} \]

The polyalkoxyaminoalkoxycycloaminosilanes have been little studied, and the intramolecular condensation of this type has not been sufficiently investigated.

The tertiary alkoxysilanes are widely used in industry, owing to their ability to impart water-repellent properties to most materials. For instance, treatment of a clean glass surface with a 1% solution of di-tert-butoxydiaminosilane in a dry hydrocarbon solvent, followed by heating to 100 - 150°C for 1 to 2 hours, makes that surface completely unwettable by water. The same effect may be attained by using tertiary alkoxychlorosilanes or tertiary alkylchlorosilanes. In these cases,
however, the volatile by-product is HCl instead of ammonia, so that this treatment cannot be applied to acid-sensitive materials, such as cellulose, for instance.

The alkoxyaminosilanes may be applied in the vapor form, in the form of undiluted liquids, or together with solvents. The choice of the method depends mainly on two factors, the character of the material to be treated, and the nature of the equipment used. For treating most materials it is best of all to use them in the form of diluted dilutions in inert solvents, or in the form of aqueous emulsions. The use of aminosilanes in road construction as an agent to reduce the peeling of the asphalt from the stones, that is usually due to the action of moisture, has been proposed.

Figure 33 shows specimens of asphalt (binding the rock) under the action of moisture on them. Figure (a) shows a specimen treated with tertiary alkoxyaminosilane, while Fig.(b) shows an untreated specimen.

**Alkyl-(Alkyl)-Aminohalosilanes**

The aminohalosilanes are products of the incomplete aminolysis of tetrahalo compounds of silicon or of halo-substituted aminosilanes, which, for instance, in the case of the chlorine derivatives, form the following series:

![Fig.33 - External View of Asphalt Specimens after the Action of Moisture](image)

- a - Specimen treated with tert-alkoxyaminosilane; b - Untreated specimen

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where R is an alkyl or aryl radical.

Diethylaminotrichlorosilane is prepared by reacting 2 moles of diethylamine and 1 mol of SiCl₄:

\[2\text{C}_2\text{H}_5\text{NH} + \text{SiCl}_4 \rightarrow \text{C}_2\text{H}_5\text{NCl}_3 + (\text{C}_2\text{H}_5)_2\text{N} \cdot \text{HCl}\]

The reaction is vigorous.

A solid mass is formed, which is washed with ether in the flask, filtered, and distilled in vacuum, yielding pure diethylaminotrichlorosilane, a colorless, mobile liquid, fuming in the air; boiling point 104°C (80 mm). Dibutylaminotrichlorosilane is prepared in the same way. It is a colorless liquid, boiling at 120°C (30 mm), that becomes slightly turbid in the air and throws down a solid, gelatinous mass. It is gradually decomposed by water.

The aryl derivatives of the chloroaminosilanes are prepared by the action of aniline on SiCl₄ in dry benzene solution. The reaction liberates considerable heat, forming a mixture of difficultly separable compounds.

\[\text{SiCl}_4 + 4\text{C}_6\text{H}_5\text{NH}_2 \rightarrow \text{C}_6\text{H}_5\text{Si}((\text{C}_6\text{H}_5)\text{NH})_2 + 2\text{C}_6\text{H}_5\text{NH}_2 \cdot \text{HCl}\]

Diphenylaminodichlorosilane in the pure state has not yet been isolated, owing to the considerable viscosity of the reaction products. These compounds have been very little studied. No products of the reactions between secondary arylamines and SiCl₄ have been prepared. The alkyl-(aryl)-aminohalosilanes are decomposed by water, forming silicon dioxide:

\[\text{C}_6\text{H}_5\text{Si}((\text{C}_6\text{H}_5)\text{NH})_2 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 2\text{C}_6\text{H}_5\text{NH}_2 + 2\text{HCl}\]

F-TS-9191/V 650
Alkyl-(Aryl)-Iminosilanes

The alkyl- and aryliminosilanes may be regarded as derivatives of such inorganic compounds as nitrylsilane and diiminosilane.

Nitrylsilane, HSiN, is an analog of HCN, and the possibility of preparing it by the reaction of silicochloroform and ammonia was pointed out as far back as 1899 (Bibl.35).

Somewhat later, nitrylsilane was prepared by other investigators, who conducted this reaction in an atmosphere of hydrogen (Bibl.34). The reaction is very vigorous, and requires cooling:

$$\text{HSiCl}_3 + 4\text{NH}_3 \rightarrow \text{HSiN} + 3\text{NH}_4\text{Cl}$$

The isolation of nitrylsilane is very complicated, owing to the difficulty of removing the ammonia from the reaction products, and to the ease with which silicodiimine is formed from nitrylsilane and ammonia.

$$\text{HSiN} + \text{NH}_3 \rightarrow \text{Si(NH)}_2 + \text{H}_2$$

The complete removal of the ammonia is effected in vacuo at $100^\circ\text{C}$.

Diiminosilane may be regarded as the amide of nitrylsilane, $N = \text{SiNH}_2$. It is easily formed by the reaction of SiCl$_4$ with ammonia, and was first prepared by means of this reaction (Bibl.10). It is believed to be tautomeric

$$\begin{align*}
\text{Si}^\text{NH} & \leftrightarrow \text{N} = \text{SiNH}_2, \\
\text{I} & \quad \text{II}
\end{align*}$$

like the tautomerism of its carbon analog, carbodiimide and cyanamide:

$$\begin{align*}
\text{C}^\text{NH} & \leftrightarrow \text{N} = \text{CNH}_2, \\
\text{I} & \quad \text{II}
\end{align*}$$

Diiminosilane has been described in detail by Leufeld, who prepared it from a benzene
solution of SiCl₄ and ammonia (Bibl.35). In the first stage, Si(NH₂)₄, tetraamino-
silane is formed, which easily liberates ammonia, giving the diimine.

\[ \text{SiCl}_4 + 4\text{NH}_3 \rightarrow \text{Si(NH}_2)_4 + 4\text{HCl} \]

\[ \text{Si(NH}_2)_4 \rightarrow 2\text{NH}_3 + \text{Si(NH)}_3 \]

It has been established by a number of analyses that diiminosilane is the principal
product of the reaction, in the absence of moisture and air. It is always obtained
mixed with ammonium chloride. Other workers have observed a similar reaction (Bibl.
36). Diiminosilane is also obtained by the action of nitrogen on calcium silicide
(Bibl.37). In this case, a mixture of compounds is formed: CaSiN₂ and Ca(SiN)₂.
Under the action of HCl, calcium silanamide is decomposed, forming iminosilane:

\[ \text{CaSiN}_2 + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{Si(NH)}_3 \]

Diiminosilane and its derivatives are likewise easily prepared by reacting silicon
disulfide, SiS₂, with ammonia at a low temperature (Bibl.38):

\[ \text{SiS}_2 + 4\text{NH}_3 \rightarrow \text{Si(NH)}_3 + 2\text{NH}_3\text{SH} \]

The same authors also prepared diiminosilane by the reaction of sulfodichlorosilane
with ammonia:

\[ \text{SSiCl}_2 + 5\text{NH}_3 \rightarrow \text{Si(NH)}_3 + 2\text{NH}_3\text{Cl} + \text{NH}_3\text{SH} \]

and also by washing the reaction products of SiCl₄ and ammonia with liquid ammonia,
in which diiminosilane is readily soluble:

\[ \text{SiCl}_4 + 6\text{NH}_3 \rightarrow \text{Si(NH)}_3 + 4\text{NH}_3\text{Cl} \]

Nitrylsilane, HSiN, is a white powder with a sharp odor, which is easily con-
verted by water into a polymeric product of the composition (HSiO₁.₅)ₙ. The forma-
tion of the polymer is believed to take place in the following way:
\[
\text{HSiN} + 3\text{H}_2\text{O} \rightarrow \text{HSi(OH)}_3 + \text{NH}_3
\]

\[
n\text{HSi(OH)}_3 \rightarrow (\text{HSiO}_2)_n + 1.5n\text{H}_2\text{O}
\]

Under the action of an alkali, nitrylsilane evolves hydrogen:

\[
\text{HSiN} + 4\text{NaOH} \rightarrow \text{Si(ONa)}_4 + \text{NH}_3 + \text{H}_2
\]

Diiminosilane in the pure condition has the form of feathery flakes, which gradually decompose under the action of the moisture of the air, forming silicon dioxide and ammonia.

Under the action of water, decomposition is instantaneous and liberates a large quantity of heat. When heated up to 1000°C, diiminosilane remains unchanged, but at temperatures above 1000°C it gives off ammonia, forming dinitrylaminodisilane:

\[
2\text{Si(NH)}_3 \rightarrow \text{N} \equiv \text{Si} - \text{NH} - \text{Si} \equiv \text{N} + \text{NH}_3
\]

which is a very stable white solid. When dinitrylaminodisilane is heated above 1200°C, it gives off ammonia and forms the silicon nitride \( \text{N}_4\text{Si}_3 \).

Under the action of HCl, diiminosilane, like tetraamino disilane, does not form salts, but decomposes, forming \( \text{SiCl}_4 \):

\[
\text{Si(NH)}_3 + 6\text{HCl} \rightarrow \text{SiCl}_4 + 2\text{NH}_4\text{Cl}
\]

Hexachlorodisilane, \( \text{Si}_2\text{Cl}_6 \), reacts with dry ammonia to give dianinodimino disilane (Bibl.39). The reaction takes place even at low temperatures:

\[
\text{Si}_2\text{Cl}_6 + 10\text{NH}_3 = 6\text{NH}_4\text{Cl} + \text{Si}_2\text{N}_6\text{H}_6
\]

This compound is believed to have the following structure:

\[
\text{NH}_3 \quad \text{Si} \quad \text{NH}_3
\]

\[
\text{NH} \quad \text{Si} \quad \text{NH}
\]
When the temperature is increased to -10°C, a molecule of ammonia is split off from the diaminodiiminodisilane, forming a different compound: triiminodisilane, which has the structure

\[
\text{HN} = \text{Si} - \text{Si} = \text{NH} \\
\text{NH}
\]

In the presence of moisture, even in traces, triiminodisilane decomposes with flashes and strong heating. When it is heated on a spatula, it explodes.

Triiminodisilane is a bulky white solid, readily soluble in liquid ammonia. It is rather stable at room temperature. It decomposes above 400°C with cleavage of ammonia, forming a polymeric silicon nitride:

\[
\text{HN} = \text{Si} - \text{Si} = \text{NH} \rightarrow (\text{Si}_3\text{N}_2)_n + n\text{NH}_3
\]

Triiminodisilane is distinguished by extreme sensitivity to moisture. It should be noted that all compounds containing the Si – N bond are easily hydrolyzed by water and decomposed by HCl:

\[
\begin{align*}
\text{R}_3\text{Si(NHR)}_n + 2\text{H}_2\text{O} & \rightarrow \text{Si}(_2\text{H})_3 + 2\text{RNH}_3 \\
\text{R}_3\text{Si(NHR)}_n + 4\text{HCl} & \rightarrow \text{R}_3\text{SiCl}_3 + 2\text{RNH}_3 \cdot \text{HCl}
\end{align*}
\]

The above described compounds of silicon and nitrogen, in contrast to the analogous carbon compounds, are extremely unstable substances (Bibl.1), and instead of monomeric, highly volatile compounds, high-polymer products are formed in this case.

Diaminodiiminodisilane may be considered the analog of diaminodiiminoethane (Bibl.40).

\[
\text{NH}_3 \quad \text{C} - \text{C} \quad \text{NH}_3
\]

but, in contrast to diaminodiiminoethane, it is immediately broken down by water, forming polymeric silicon dioxide as a stable end product.

Attempts to prepare alkyl and aryl derivatives of nitrylsilane, of the type
RSiN, have up to now been unsuccessful (Bibl.41). By bromination of tetrapheny氨基silane, Reynolds has prepared the only known haloaryltrimilane, $\text{Br}_2\text{C}_6\text{H}_3\text{SiN}$ (Bibl.42):  

$$\text{Si(\text{NH}_4\text{C}_6\text{H}_3)}_4 \cdot 3\text{Br}_2 \rightarrow \text{Si(N\equiv\text{I-ICl})_3\text{Br}_2} + 3\text{C}_6\text{H}_5\text{NH}_3 + 4\text{HBr}$$

As tetraaminosilane is converted on heating into the more stable diiminosilane, so tetraphenylaminosilane, when heated, passes over into di-(phenylimino)-silane:

$$\text{Si(\text{NH}_4\text{C}_6\text{H}_3)}_4 \rightarrow \text{Si(N\equiv\text{I-ICl})_3\text{Br}_2} + 2\text{NH}_3$$
$$\text{Si(\text{NH}_4\text{C}_6\text{H}_3)}_4 \rightarrow \text{Si(\text{NC}_6\text{H}_5)_2} + 2\text{C}_6\text{H}_5\text{NH}_2$$

Di-(phenylimino)-silane should apparently be regarded as an isomer of diphenylaminotrisilane:

$$\text{Si(\text{NC}_6\text{H}_5)_2} \quad \text{N\equiv\text{Si-N(\text{C}_6\text{H}_5)_3}}$$

as aminonitrylsilane is isomeric with diiminosilane. This has been confirmed by Reynolds, who has established the formation of two modifications of di-(phenylimino)-silane, one compound that is soluble in benzene (sym-$\text{Si(\text{NC}_6\text{H}_5)_2}$), and an insoluble compound whose structure has not been established.

Di-(phenylimino)-silane is best prepared by vacuum distillation of tetraphenylaminosilane, which, under these conditions, splits off aniline, and passes, by way of di-phenylamino-phenliminosilane, into di-phenylimino-silane:

$$\text{Si(\text{NH}_4\text{C}_6\text{H}_3)_4} \rightarrow (\text{C}_6\text{H}_5\text{NH})_3\text{Si=N-\text{C}_6\text{H}_5} + \text{C}_6\text{H}_5\text{NH}_2$$
$$\text{(C}_6\text{H}_5\text{NH})_3\text{Si=N-\text{C}_6\text{H}_5} \rightarrow (\text{C}_6\text{H}_5\text{N})_3\text{Si} + \text{C}_6\text{H}_5\text{NH}_2.$$

Then reacted with phenyl mustard oil, di-phenylimino-silane forms a compound that is probably of the following structure:
Heating of di-(phenylamino)-silane produces a compound whose structure may probably be represented by the following formula:

\[
\begin{align*}
\text{Si} & \quad \text{N} - \text{C}_6\text{H}_5 \\
\text{Si} & \quad \text{N} - \text{C}_6\text{H}_5 \\
\text{Si} & \quad \text{N} - \text{C}_6\text{H}_5
\end{align*}
\]

This compound, on further heating with dry ammonia, splits off two molecules of aniline and passes over into \( \text{Si}_2(\text{NH})_2 - \text{N} - \text{C}_6\text{H}_5 \).

These compounds are derivatives of the silicon nitride \( \text{Si}_2\text{N}_3 \) that has been discussed above.

Di-(phenylimino)-silane is prepared by the action of aniline on tetra-thiocy-anatosilane on heating, since cleavage of two molecules of aniline from the tetra-phenylaminosilane initially formed results:

\[
\text{Si}(\text{CNS})_4 + 8\text{C}_6\text{H}_5\text{NH}_2 \rightarrow \text{Si}(\text{NHCl})_4 + 4\text{C}_6\text{H}_5\text{NH}_2\cdot\text{HCNS}
\]

The reaction of pyrrolopotassium with \( \text{SiCl}_4 \) yields a tetra-derivative of pyrrol, which is the only known example of an organosilicon compound with four nitrogen-containing rings (Bibl.43).

Tetrapyrrolosilane crystallizes in colorless prisms with the melting point of \( 173.4^\circ \text{C} \), difficultly soluble in petroleum ether, but readily soluble in benzene, carbon disulfide, dichloroethane, and ether. It carbonizes on heating.
Other cyclic organic nitrogen compounds, such as pyridine, quinoline, etc., form only addition products.

**Alkyl-(Aryl)-Aminoalkylsilanes and Alkoxyaminoalkylsilanes**

Organosilicon compounds containing \( \text{Si} - \text{C} - \text{N} \) groups in their molecules may be prepared by the action of dry ammonia or amines on compounds of the general formula \( \text{R}_3\text{SiCH}_2\text{X} \), where \( \text{R} \) is an alkyl, aryl, or alkoxy group, and \( \text{X} \) is a halogen atom:

\[
\text{R}_3\text{SiCH}_2\text{Cl} + \text{NH}_3 \rightarrow \text{R}_3\text{SiNHCH}_2\text{Cl} + \text{HCl}
\]

In the presence of water or alcohol, cleavage of the \(-\text{CH}_2\text{Cl}\) group is observed. For the more complete substitution of the halogen, use of a twenty-fold excess of ammonia, or a threefold excess of amine, is recommended. The reaction proceeds at 120°C, under pressure, forming 50 - 70% of primary amines, 20 - 30% of secondary amines, and small quantities of unstable substances. Tertiary amines of the structure \( \text{R}_3\text{SiCH}_2\text{N} \) are unstable, decomposing in air, and it has not been possible to isolate them (Bibl.44).

When sodium amide in liquid ammonia acts on trimethylchloromethylsilane, trimethylmethylaminosilane is formed:

\[
(\text{CH}_3)\text{SiCH}_2\text{Cl} + \text{NaNH}_2 \rightarrow (\text{CH}_3)\text{SiNHCH}_2\text{Na} + \text{HCl}
\]

Distillation of this product liberates methylamine, and hexamethyldimethylaminesilane is formed:

\[
2(\text{CH}_3)\text{SiNHCH}_2 \rightarrow [(\text{CH}_3)\text{Si}]_2\text{NCH}_2 + \text{CH}_3\text{NH}_2
\]

Certain amino derivatives of the siloxanes, containing the group \( \text{Si} - \text{O} - \text{Si} - \text{C} - \text{NR}_2 \), may be prepared in three ways:

1. Di-(chloromethyl)-tetramethylsiloxane is treated with ammonia or an amine, yielding a mixture of products difficult to separate.
2. Methyl(diethoxy)aminomethylsilane is hydrolyzed in aqueous or aqueous-alcoholic solutions, forming a thermoplastic polymer soluble in water.

Triethoxyaminomethylsilane under these conditions is transformed into a white amorphous water-soluble powder.

3. Compounds of the type \((\text{CH}_3)_3\text{SiCH}_2\text{NR}_2\), (where \(R\) may be the group \((\text{CH}_3)_3\text{SiCH}_2, \text{H}, \text{or an alkyl group}) are heated with an excess of sulfuric acid at 100 - 110\(^\circ\)C for 6 to 36 hours. Cleavage of methane from the trimethylaminomethylsilane takes place under these conditions.

A synthesis of organosilicon compounds containing p-dimethylaminophenyl groups has been described. Such compounds are prepared by adding two or three equivalents of p-dimethylaminophenyllithium to \(\text{SiCl}_4\). The mixture so formed is then immediately hydrolyzed, yielding di-(p-dimethylaminophenyl)-silanediol (Bibl.45). Under these conditions, tri-(p-dimethylaminophenyl)-chlorosilane and tri-(p-dimethylaminophenyl)-silanol may be prepared in satisfactory yield (Bibl.46).

Treatment of tri-(p-dimethylaminophenyl)-silanol with concentrated formic or acetic acid forms light bluish vitreous polymeric substances.

Preparation of Triphenyl-p-dimethylaminophenylsilane. To an ethereal solution of 0.15 mol of \(\text{SiCl}_4\), an ethereal solution of 0.45 mol of phenyllithium is added, forming triphenylchlorosilane.

To this solution 0.10 mol of p-dimethylaminophenyllithium is slowly added. The reaction is conducted in an atmosphere of nitrogen.

After completion of the reaction, the reaction mixture is treated with water to dissolve the LiCl. The ethereal layer is separated, dried, and evaporated. A solid product is thus isolated, and is recrystallized from petroleum ether. The crystals melt at 144 - 146\(^\circ\)C, and consist of triphenyl-p-dimethylaminophenylsilane. The by-product tetraphenylsilane, melting point 233 - 235\(^\circ\)C, is also formed.

Preparation of Di-(p-dimethylaminophenyl)-silanediol. in a nitrogen atmosphere 0.17 mol of p-dimethylaminophenyllithium is added to a solution of 9.52 g (0.056 mol)
<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c) °C</th>
<th>d) °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aminomethyltrimethylsilane</td>
<td>(CH₃)₂SiCH₂NH₂</td>
<td></td>
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</tr>
<tr>
<td>Aminomethyltrimethylsilanehydrochloride</td>
<td>(CH₃)₂SiCH₂NH₂·HCl</td>
<td></td>
<td>240—241</td>
</tr>
<tr>
<td>Aminomethyltrimethylenesulfite</td>
<td>(CH₃)₂SiCH₂NH₄·H₂SO₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aminomethyltrimethylenesulfate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methylaminomethyltrichlorosilane</td>
<td>(CH₃)₂SiCH₂NH₂·H₂SO₄</td>
<td></td>
<td>213—216</td>
</tr>
<tr>
<td>Methylaminomethyltrimethylsilane</td>
<td>(CH₃)₂SiCH₂NH₂CH₃</td>
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<td>Methylaminomethyltrichlorosilanehydrochloride</td>
<td>(CH₃)₂SiCH₂NHCH₃·HCl</td>
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<td>Dimethylaminomethyltrimethylsilane</td>
<td>(CH₃)₂SiCH₂N(CH₃)₂</td>
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<tr>
<td>Dimethylaminomethyltrichlorosilanehydrochloride</td>
<td>(CH₃)₂SiCH₂N(CH₃)₂·HCl</td>
<td>195—196</td>
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<tr>
<td>Dimethylaminomethyltrimethyleneproplumbate</td>
<td>(CH₃)₂SiCH₂N(CH₃)₂·HBr</td>
<td>260—262</td>
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<tr>
<td>Isopropylaminomethyltrimethylsilane</td>
<td>(CH₃)₂Si(CH₂)₃NH(CH₃)₂</td>
<td>241.5—242.5</td>
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<tr>
<td>Isopropylaminomethyltrichlorosilanehydrochloride</td>
<td>(CH₃)₂SiCH₂NHCH(CH₃)₂·HCl</td>
<td>136—137</td>
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<tr>
<td>Tert-butylaminomethyltrimethylsilane</td>
<td>(CH₃)₂SiCH₂NH(CH(CH₃)₃)</td>
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<td>Phenylaminomethyltrimethylsilane</td>
<td>(CH₃)₂SiCH₂NHCH₂C₆H₅</td>
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<tr>
<td>p-Nitrobenzoylaminomethyltrimethylsilane</td>
<td>(CH₃)₂SiCH₂NC₆H₄NO₂</td>
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<td>Cyclohexylaminomethyltrimethylsilane</td>
<td>(CH₃)₂SiCH₂NHCH₂C₆H₄</td>
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<tr>
<td>Cyclohexylaminomethyltrichlorosilanehydrochloride</td>
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<td>285—289</td>
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<tr>
<td>Octadecylaminomethyltrimethylsilane</td>
<td>(CH₃)₂SiCH₂NH₄C₁₈H₃₇</td>
<td></td>
<td>193—194</td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Melting point; d) Boiling point;
<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c) °C</th>
<th>d) °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octadecylaminomethyltrimethylsilane</td>
<td>(CH₉)₂Si(CH₂)NHCH₃H₂H₂·HCl</td>
<td>26—32</td>
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<tr>
<td>Hexamethylene-aminomethylenedisilane</td>
<td>(CH₂)₃Si(CH₂)₂NH</td>
<td></td>
<td>170,5</td>
</tr>
<tr>
<td>Hexamethylaminoethylhydrochloride</td>
<td>(CH₂)₃Si(CH₂)₂NH·HCl</td>
<td></td>
<td>158—159</td>
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<tr>
<td>Aminomethyldimethylethylsilane</td>
<td>C₆H₅Si(CH₂)₃CH₂NH₂</td>
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<td>67,5</td>
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<td>Aminomethyltriethylsilane</td>
<td>(C₆H₅)₃SiCH₂NH₂</td>
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<td>93</td>
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<tr>
<td>Hexaethyl-(methyleneaminomethylene)-disilane</td>
<td>(C₆H₅)₃SiCH₂NH</td>
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<td>117</td>
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<tr>
<td>Aminomethyldimethylphenylsilane</td>
<td>C₆H₅Si(CH₂)₃CH₂NH₂</td>
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<td>196—200</td>
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<td>Aminomethyldimethylphenylsilanehydrochloride</td>
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<td>215,2</td>
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<td>Diphenyltetramethyl-(methyleneaminomethylene)disilane</td>
<td>(C₆H₅)₃Si(CH₂)₃CH₂NH₂</td>
<td>247—249</td>
<td></td>
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<tr>
<td>Diphenyltetramethyl-(methyleneaminomethylene)-disilanehydrochloride</td>
<td>(C₆H₅)₃Si(CH₂)₃CH₂NH·HCl</td>
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<td>121—126</td>
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<tr>
<td>Di-(aminomethyl)-tetramethyldisiloxane</td>
<td>(CH₂)₃SiCH₂NHCH₂Si(CH₂)₂</td>
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<td>152</td>
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<td>Octamethylcyclodi-(methyleneaminomethylene)-disiloxane</td>
<td>(CH₂)₃SiCH₂NHCH₂Si(CH₂)₂</td>
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<td>245</td>
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<td>Di-(isopropylaminomethyl)tetramethyldisiloxane</td>
<td>(CH₃)₂Si—CH₂</td>
<td></td>
<td>187,5</td>
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<td>Tetramethylcyclo-(isopropylaminodimethylene)-disiloxane</td>
<td>(CH₃)₂Si—CH₂</td>
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</table>
Table 74

Physical Properties of Alkyl-(Aryl)-Aminomethyl-Methylalkoxysiloxanes (Hibb.48)

<table>
<thead>
<tr>
<th>a) Name</th>
<th>b) Formula</th>
<th>c) Boiling point</th>
<th>d) Specific gravity</th>
<th>e) Refractive index</th>
<th>f) Molecular refraction</th>
<th>g) Found</th>
<th>h) Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenylaminomethyl-(methyl)-dimethylsilane</td>
<td>C₆H₄NHCH₂(CH₂)₂Si(OCH₃)₂</td>
<td>139-141 (15 mm)</td>
<td>1.052</td>
<td>1.5120</td>
<td>60.2</td>
<td>59.7</td>
<td></td>
</tr>
<tr>
<td>Phenylaminomethyl-(methyl)-diethoxysilane</td>
<td>C₆H₄NHCH₂(CH₂)₂Si(OCH₂)₂</td>
<td>152-153 (16 mm)</td>
<td>1.002</td>
<td>1.4975</td>
<td>69.8</td>
<td>68.9</td>
<td></td>
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<tr>
<td>Phenylaminomethyl-(methyl)-diisopropoxysilane</td>
<td>C₆H₄NHCH₂(CH₂)₂Si(OCH(CH₃)₂)₂</td>
<td>160-162 (16 mm)</td>
<td>0.969</td>
<td>1.4853</td>
<td>78.2</td>
<td>78.2</td>
<td></td>
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<tr>
<td>Phenylaminomethyl-(methyl)-diisobutoxysilane</td>
<td>C₆H₄NHCH₂(CH₂)₂Si(OCH₂CH(CH₃)₂)₂</td>
<td>180-182 (17 mm)</td>
<td>0.9602</td>
<td>1.4846</td>
<td>87.9</td>
<td>87.4</td>
<td></td>
</tr>
<tr>
<td>Phenylaminomethyl-(methyl)-diisomyloxy silane</td>
<td>C₆H₄NHCH₂(CH₂)₂Si(OCH₂CH₂CH(CH₃)₂)₂</td>
<td>162-164 (8 mm)</td>
<td>0.9502</td>
<td>1.4832</td>
<td>97.0</td>
<td>96.7</td>
<td></td>
</tr>
<tr>
<td>Ethylphenylaminomethyl-(methyl)-dimethoxysilane</td>
<td>C₆H₅(C₂H₅)NHCH₂(CH₂)₂Si(OCH₂)₂</td>
<td>151-154 (23 mm)</td>
<td>1.024</td>
<td>1.5131</td>
<td>70.2</td>
<td>69.1</td>
<td></td>
</tr>
<tr>
<td>Ethylphenylaminomethyl-(methyl)-diethoxysilane</td>
<td>C₆H₅(C₂H₅)NHCH₂(CH₂)₂Si(OCH₂)₂</td>
<td>130-136 (9 mm)</td>
<td>0.9926</td>
<td>1.4978</td>
<td>78.8</td>
<td>78.4</td>
<td></td>
</tr>
<tr>
<td>Ethylphenylaminomethyl-(methyl)-diisopropoxysilane</td>
<td>C₆H₅(C₂H₅)NHCH₂(CH₂)₂Si(OCH(CH₃)₂)₂</td>
<td>150-156 (15 mm)</td>
<td>0.9723</td>
<td>1.4900</td>
<td>87.7</td>
<td>87.6</td>
<td></td>
</tr>
<tr>
<td>Ethylphenylaminomethyl-(methyl)-diisobutoxysilane</td>
<td>C₆H₅(C₂H₅)NHCH₂(CH₂)₂Si(OCH₂CH(CH₃)₂)₂</td>
<td>171-172 (14 mm)</td>
<td>0.9536</td>
<td>1.4890</td>
<td>96.3</td>
<td>96.9</td>
<td></td>
</tr>
<tr>
<td>Ethylphenylaminomethyl-(methyl)-diisomyloxy silane</td>
<td>C₆H₅(C₂H₅)NHCH₂(CH₂)₂Si(OCH₂CH₂CH(CH₃)₂)₂</td>
<td>167-168 (7 mm)</td>
<td>0.9482</td>
<td>1.4862</td>
<td>106.3</td>
<td>106.2</td>
<td></td>
</tr>
<tr>
<td>Aminomethyldi-(methyl)-ethoxysilane</td>
<td>C₆H₄OSi(CH₃)₂CH₂NH₂</td>
<td>131.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,2-Tetramethyl-1,2-dioethoxy-(methyleneaminomethylene)-disilane</td>
<td>(C₆H₄O)Si(CH₂)₂CH₂NH₂HCl</td>
<td>M. P. 183-187</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenylaminomethyldi-(methyl)-ethoxysilane</td>
<td>(C₆H₄O)Si(CH₂)₂CH₂NH₄H₄</td>
<td>160-170</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
of SiCl₄ in ether over a period of 2 hours, holding the temperature of the reaction mixture between -15°C and -20°C.

The solution is stirred 30 min at room temperature, and is then hydrolyzed by water. The ethereal layer is separated and dried, and the ether is distilled off. The light bluish deposit so obtained is crystallized from a mixture of benzene and petroleum ether, yielding di-(p-dimethylaminophenyl)-silanediol, melting point 173-174°C.

A number of α-(aminomethyl)-methyldialkoxy silanes (Bibl.47) and -(phenylaminomethyl)-methyldialkoxy silanes (Bibl.48) have recently been described. The former compounds were prepared by the action of ammonia on halomethylethoxysilanes; the latter, by the action of aniline or ethylaniline on chloromethylenethoxysilanes:

\[
\begin{align*}
(+\text{RO})₂\text{Si} & \text{CH}_₂\text{Cl} + 2\text{H}_₂\text{NC}_₆\text{H}_₄ \rightarrow (+\text{RO})₂\text{Si} \text{CH}_₂\text{NH}_₂\text{C}_₆\text{H}_₄ + \text{C}_₆\text{H}_₄\text{NH}⁺\text{HCl} \\
(+\text{RO})₂\text{Si} & \text{CH}_₂\text{Cl} + 2\text{NH}_₂\text{C}_₆\text{H}_₄ \rightarrow (+\text{RO})₂\text{Si} \text{CH}_₂\text{N} \text{C}_₂\text{H}_₄ + \text{C}_₆\text{H}_₄\text{NH}⁺\text{HCl}
\end{align*}
\]

The reaction is conducted at atmospheric pressure. The yield of the reaction products is good, but decreases with increasing number of alkoxy groups.

Preparation of (phenylaminomethyl)-methyldialkoxy silanes (Bibl.48). In a flask with reflux condenser are placed 0.5 mol of α-chloromethylenethoxysilane, 1.5 mol of aniline, and the mixture is heated 3 to 4 hours, with stirring, at 130-140°C.

A precipitate of aniline hydrochloride is thrown down during the reaction, which is removed by filtration, and washed with benzene; the filtrate is distilled at reduced pressure, yielding (phenylaminomethyl)-methyldimethoxysilane, boiling point 139-141°C (15 mm). The yield is 48% of theoretical. The synthesis of (phenylaminomethyl)-methyldiethoxysilane is similar.

Table 73 gives the physical properties of alkyl-(aryl)-aminoalkyldilanes and alkyl-(aryl)-aminoalkylsiloxanes; and Table 74 those of alkyl-(aryl)-aminomethyl-
methylalkoxysilanes.

**Silicon Isocyanates**

**Preparation of Isocyanatosilanes**

Organosilicon compounds containing the isocyanate group, \(-N=C=O\), attached to a silicon atom, have been synthesized a few years ago. The literature describes alkylisocyanatosilanes, arylisocyanatosilanes, and alkoxyisocyanatosilanes. These compounds are obtained on the reaction between alkyl- or arylchlorosilanes and silver isocyanate:

\[
\begin{align*}
\text{CH}_2\text{SiCl}_3 + 3\text{CONAg} & \rightarrow \text{CH}_2\text{Si(NCO)}_3 + 3\text{AgCl} \\
\text{C}_4\text{H}_5\text{SiCl}_3 + 3\text{CONAg} & \rightarrow \text{C}_4\text{H}_5\text{Si(NCO)}_3 + 3\text{AgCl} \\
(R)\text{SiCl}_3 + 3\text{CONAg} & \rightarrow (R)\text{Si(NCO)}_3 + 3\text{AgCl}
\end{align*}
\]

Mono- and diisocyanato derivatives are similarly prepared.

Isocyanato derivatives are easily prepared in a medium of solvents that do not react with alkyl- and arylchlorosilanes, nor with alkyl- and arylisocyanatosilanes. Hydrocarbons of the aliphatic and aromatic series may be used as such solvents: benzene, toluene, propylbenzene, xylene, as well as benzine and other solvents (Bibl. 49). The reaction temperature is 80 - 90°C. Silver isocyanate in 10 - 25% excess is used in the reaction.

**Preparation of Methylisocyanatosilane.** Into a solution of 148 g of methyltrichlorosilane in benzene (a 25% solution), 490 g of silver isocyanate is introduced in three portions. The mixture is heated 30 min at 90°C. The suspension of silver chloride is then filtered off and washed with benzene. The methyltrisocyanatosilane is separated from the benzene solution by distillation; boiling point, 170.8°C. Yield, about 80% of theoretical.

**Preparation of Ethoxytrisocyanatosilane.** A 30% solution of ethoxytrichlorosilane in benzene is heated with an excess of silver isocyanate for 30 min at 90°C. The silver chloride is filtered off and washed with benzene. The benzene solution,
on fractional distillation, yields ethoxytriisocyanatosilane; boiling point 179.6°C. The yield is 70% of theoretical.

When SiCl₄ reacts with silver isocyanate, tetracyanatosilane and tetraisocyanatosilane are formed. Their structure is demonstrated by hydrolysis:

\[
\begin{align*}
\text{Si(NCO)}_4 + 4\text{H}_2\text{O} & \rightarrow \text{Si(OH)}_4 + 4\text{HNC}O \\
\text{Si(NCO)}_4 + 12\text{H}_2\text{O} & \rightarrow \text{Si(OH)}_4 + 4\text{NH}_2\text{HCO}_3
\end{align*}
\]

When AgNOO acts on polychlorosiloxanes, formation of octaisocynantotrisiloxane, hexaisocyanatodisiloxane, etc., occurs. The first of these products may also be prepared by cautious hydrolysis of tetraisocyanatosilane (Bibl.50).

On heating SiCl₄ and Si(NCO)₄ to 600°C, there is a rapid rearrangement reaction; and all possible compounds of the type \( \text{SiCl}_4-x\text{(NCO)}_x \) are formed. A mixture of tetra-thiocyanatosilane and tetraisocyanatosilane heated 4 hours at 140°C also undergoes rearrangement to form all possible compounds of the type \( \text{(OCN)}_x\text{Si(SCN)}_{4-x} \).

The reaction between tetraisocyanatosilane and methanol also forms a mixture of compounds of the general formula \( \text{(CH}_3\text{O)}_x\text{Si(NOO)}_{4-x} \) (Bibl.52).

\( \text{SbF}_3 \) reacts with tetraisocyanatosilane to form a mixture of products of the composition \( \text{F}_x\text{Si(NCO)}_{4-x} \) and \( \text{Sb(NOO)}_3 \).

**Physical Properties of Isocyanatosilanes**

Alkyl- and arylisocyanatosilanes are readily soluble in petroleum ether, carbon disulfide, carbon tetrachloride, benzene, and isopropylbenzene.

Methylisocyanatosilanes and n-butyltriisocyanatosilanes are colorless liquids; phenylisocyanatosilanes are crystalline substances with an unpleasant odor. The methylisocyanatosilanes easily take fire.

The methylisocyanatosilanes have an exact melting point and freezing point (without appreciable supercooling); n-butyltriisocyanatosilane has a tendency to supercooling and formation of a vitreous mass. Phenyltriisocyanatosilane has no distinct melting point, and melts at a temperature from -50°C to -20°C. Diphenylidil-
isocyanatosilane at -70°C forms crystals with a distinct melting point. Triphenylisocyanatosilane can be supercooled by more than 20°C, forming crystals with a distinct melting point. Table 75 gives the principal physical properties of alkyl- and arylisocyanatosilanes.

Alkyl- and arylisocyanatosilanes are readily converted, on heating, into vitreous substances, so that the melting points are given only approximately for a number of compounds.

Chemical Properties of Isocyanatosilanes

Under the action of water, the alkyl-(aryl)-isocyanatosilanes undergo hydrolysis. The velocity of such hydrolysis is considerably lower than that of tetraisocyanatosilane. With increasing number of organic radicals attached to the silicon atom, and with their increasing size, the rate of hydrolysis of these compounds decreases. Alkylisocyanatosilanes containing several \(-N=C=0\) groups and one large organic radical are hydrolyzed more rapidly than such compounds containing a smaller number of \(-N=C=0\) groups and two small organic radicals attached to the silicon atom; for instance, dimethyldiisocyanatosilane is hydrolyzed more slowly by water than butyltriisocyanatosilane.

The alkoxyisocyanatosilanes are more readily hydrolyzed by water than the alkyl- and arylisocyanatosilanes; while triphenylisocyanatosilane is hydrolyzed very slowly by water.

Silicon Compounds Containing Sulfur

Silicon forms with sulfur the chemical compound \(\text{SiS}_2\). In crystals of \(\text{SiS}_2\) each silicon atom is in the center of a tetrahedron of four sulfur atoms, and each sulfur atom is attached to two silicon atoms.

Such crystals have edges in common and form a chain of the following structure:
Table 75

Physical Properties of Isocyanatosilanes (Bibl.68)

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c) °C</th>
<th>d) (d^0)</th>
<th>e) (n_D^0)</th>
<th>f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetraisocyanatosilane</td>
<td>Si(NCO)₄</td>
<td>185.6</td>
<td>1.142</td>
<td>1.4610</td>
<td>—</td>
</tr>
<tr>
<td>Methyltrisocyanatosilane</td>
<td>CH₃Si(NCO)₃</td>
<td>170.8</td>
<td>1.267</td>
<td>1.4430</td>
<td>35.39</td>
</tr>
<tr>
<td>Dimethyltrisocyanatosilane</td>
<td>(CH₃)₂Si(NCO)₂</td>
<td>139.2</td>
<td>0.976</td>
<td>1.4221</td>
<td>33.6</td>
</tr>
<tr>
<td>Trimethylisocyanatosilane</td>
<td>(CH₃)₃Si(NCO)</td>
<td>91.0</td>
<td>0.867</td>
<td>1.3960</td>
<td>31.92</td>
</tr>
<tr>
<td>Ethyltrisocyanatosilane</td>
<td>C₂H₅Si(NCO)₃</td>
<td>183.5</td>
<td>1.2192</td>
<td>1.4468</td>
<td>—</td>
</tr>
<tr>
<td>Diethyltrisocyanatosilane</td>
<td>(C₂H₅)₂Si(NCO)₂</td>
<td>176.7</td>
<td>1.0223</td>
<td>1.4348</td>
<td>—</td>
</tr>
<tr>
<td>Triethylisocyanatosilane</td>
<td>C₆H₁₃Si(NCO)</td>
<td>165.1</td>
<td>0.8805</td>
<td>1.4295</td>
<td>—</td>
</tr>
<tr>
<td>Propyltrisocyanatosilane</td>
<td>(C₆H₁₃)₃Si(NCO)</td>
<td>198.2</td>
<td>1.1726</td>
<td>1.4462</td>
<td>—</td>
</tr>
<tr>
<td>Isopropyltrisocyanatosilane</td>
<td>(CH₃)₂CHSi(NCO)</td>
<td>192.0</td>
<td>1.1626</td>
<td>1.4444</td>
<td>—</td>
</tr>
<tr>
<td>n-Butyltrisocyanatosilane</td>
<td>C₄H₉Si(NCO)₃</td>
<td>215.5</td>
<td>1.141</td>
<td>1.4479</td>
<td>46.5</td>
</tr>
<tr>
<td>Phenyltrisocyanatosilane</td>
<td>C₆H₅Si(NCO)₃</td>
<td>251.9</td>
<td>1.273</td>
<td>1.5210</td>
<td>55.45</td>
</tr>
<tr>
<td>Diphenyltrisocyanatosilane</td>
<td>(C₆H₅)₂Si(NCO)₂</td>
<td>319.6</td>
<td>1.188</td>
<td>1.5675</td>
<td>73.3</td>
</tr>
<tr>
<td>Triphenylisocyanatosilane</td>
<td>(C₆H₅)₃Si(NCO)</td>
<td>372.0</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Dicyclohexyltrisocyanatosilane</td>
<td>C₆H₁₂CH₃Si(NCO)</td>
<td>111—112 (3 mm)</td>
<td>1.225</td>
<td>1.5230</td>
<td>60.2</td>
</tr>
<tr>
<td>Methoxytrisocyanatosilane</td>
<td>(CH₃O)Si(NCO)₃</td>
<td>168.4</td>
<td>1.313</td>
<td>1.4287</td>
<td>36.38</td>
</tr>
<tr>
<td>Timethoxytrisocyanatosilane</td>
<td>(CH₂O)₂Si(NCO)₂</td>
<td>152.1</td>
<td>1.208</td>
<td>1.4028</td>
<td>35.01</td>
</tr>
<tr>
<td>Trimethoxytrisocyanatosilane</td>
<td>(CH₂O)₃Si(NCO)</td>
<td>137.0</td>
<td>1.123</td>
<td>1.3839</td>
<td>33.96</td>
</tr>
<tr>
<td>Ethoxytrisocyanatosilane</td>
<td>(CH₂O)₂Si(NCO)₂</td>
<td>179.6</td>
<td>1.236</td>
<td>1.4251</td>
<td>41.0</td>
</tr>
<tr>
<td>Diethoxytrisocyanatosilane</td>
<td>(CH₂O)₃Si(NCO)</td>
<td>175.4</td>
<td>1.108</td>
<td>1.4046</td>
<td>44.7</td>
</tr>
<tr>
<td>Trisiloxane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trichlorotrisocyanatosilane</td>
<td>CCl₃Si(NCO)₃</td>
<td>152.0</td>
<td>1.437</td>
<td>1.4507</td>
<td>—</td>
</tr>
<tr>
<td>Dichlorodiisocyanatosilane</td>
<td>CCl₂Si(NCO)₂</td>
<td>117.8</td>
<td>1.437</td>
<td>1.4380</td>
<td>—</td>
</tr>
<tr>
<td>Trichloroisocyanatosilane</td>
<td>CCl₃Si(NCO)</td>
<td>86.8</td>
<td>1.445</td>
<td>1.4262</td>
<td>—</td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Melting point; d) Specific gravity; e) Refractive index; f) Molecular refraction
The structure of the SiS₂ crystal differs from that of the SiO₂ crystal. In crystals of silicon sulfide the tetrahedra are joined by their common edges, while the joining of the tetrahedra in SiO₂ is by their common corners. It is customarily considered that the transition from common corners to common edges is connected with an increase in the covalent character of the bond.

The compounds of silicon with sulfur are polymeric, and therefore SiS₂ is a low-volatile solid substance and forms long white needles with a silky luster. The crystals melt at 1090°C and burn with great difficulty in oxygen. This substance was first prepared by Berzelius by the action of sulfur vapor on silicon at a white heat. It was later prepared by the reaction of CS₂ and silicon (Bibl.53).

Silicon sulfide is slowly hydrolyzed by water, and rapidly by alkalies, forming orthosilicic acid and H₂S.

It may also be prepared by fusing silicon with sulfur at a high temperature, or by the action of CS₂ on silicon. The reaction is effected by heating crystalline silicon in carbon disulfide vapor, forming two products, the yellow powder SiS₂ and the yellowish powder SiSO. It must be noted, however, that this information is based on works published in the second half of the last century, which contain data that are insufficiently convincing with respect to the characteristics of the products obtained. The investigators probably obtained not pure SiS₂ but products containing impurities. This view is also confirmed by the fact that subsequent researches failed to find SiSO on calcining the crystalline reaction product.

In 1846 the action of H₂S on SiCl₄ in a porcelain tube at high temperatures yielded liquid products (Bibl.54), to which the author assigned the composition SiSCl₂, Si₂S₂Cl₄, but Friedel and Crafts showed that these products were not formed, but trichloromercaptosilane:
\[
\text{SiCl}_4 + \text{H}_2\text{S} \rightarrow \text{Cl}_2\text{SiSH} + \text{HCl}
\]

which is decomposed by water:

\[
\text{Cl}_2\text{SiSH} + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + \text{H}_2\text{S} + 3\text{HCl}
\]

**Thio-Esters of Orthosilicic Acid**

When water-free alcohols act on trichloromercaptosilane, organic silicon derivatives containing a thio group are formed:

\[
\text{Cl}_3\text{SiSH} + 3\text{C}_2\text{H}_5\text{OH} \rightarrow (\text{C}_2\text{H}_5\text{O})_3\text{SiSH} + 3\text{HCl}
\]

The ethyl ester of orthosilicic acid is formed as a by product:

\[
\text{Cl}_3\text{SiSH} + 4\text{C}_2\text{H}_5\text{OH} \rightarrow (\text{C}_2\text{H}_5\text{O})_4\text{Si} + 3\text{HCl} + \text{H}_2\text{S}
\]

Organosilicon compounds containing sulfur have been prepared by the reaction of phenylmercaptan with SiCl₄ (Bibl.55):

\[
\text{C}_6\text{H}_5\text{SH} + \text{SiCl}_4 \rightarrow \text{C}_6\text{H}_5\text{SSiCl}_3 + \text{HCl}
\]

Trichloro-(phenylthio)-silane is a liquid that easily decomposes in air, and with particular ease under the action of water. When ethymercaptan is heated with SiCl₄, the formation of trichloroethylsilane is possible.

Tetra-(thiophene)-silane has been prepared by heating a 40% solution of SiCl₄ in ether with a solution of α-thiophenemagnesium iodide in ether (Bibl.56):

\[
4\text{C}_2\text{H}_5\text{SMgI} + \text{SiCl}_4 \rightarrow \text{Si(C}_2\text{H}_5\text{S})_4 + 4\text{MgClI}
\]

Tetra-(thiophene)-silane is a crystalline substance with a melting point of 135.5°. It is soluble in hot ethanol, ether, and benzene, insoluble in water, and difficultly soluble in cold ethanol.

Table 76 (cf. page 670) gives the physical properties of the thio-esters of
orthosilicic acid.

An interesting reaction takes place when mercaptans act on unsaturated silanes in the presence of a peroxide. The mechanism of the reaction between mercaptans and silanes containing unsaturated radicals is assumed to be analogous to the well known reaction for organic compounds (Bibl. 57):

\[ \text{RSH + peroxide} \rightarrow \text{RS.} \]  
\[ \text{RS} + \text{R'CH}=\text{CH} \rightarrow \text{R'CH-CH}_2\text{SR} \]  
\[ \text{R'CH-CH}_2\text{SR} + \text{RSH} \rightarrow \text{R'CH-CH}_2\text{SR} + \text{RS. etc.} \]

The reaction between trimethylallylsilane and thioglycolic acid follows the equation:

\[ (\text{CH}_3)_2\text{SiCH}==\text{CH} + \text{HSCH}_2\text{COOH} \rightarrow (\text{CH}_3)_2\text{SiCH}_2\text{CH}=\text{CH}_2\text{SCH}_2\text{COOH} \]

The chlorine in an organic radical attached to the silicon atom also reacts with the thio group according to the equation:

\[ (\text{C}_6\text{H}_{11})_3\text{SiCH}_2\text{CH}_2\text{Cl} + \text{HSCH}_2\text{COOH} \rightarrow (\text{C}_6\text{H}_{11})_3\text{SiCH}_2\text{CH}_2\text{SCH}_2\text{COOH} + \text{HCl} \]

As a result of the reaction between dimercaptans and dialkylsilanes, viscous, oily products are formed.

A sulfur atom in an organic radical in the β-position with respect to the silicon atom does not weaken the Si - C bond; this bond is not broken under the action of acids or alkalies.

**Preparation of Carboxymethylthioethyltrimethylsilane.** A mixture of 10 g of allyltrimethylsilane and 15 g of 98% thioglycolic acid is held 10 - 15 min. in an open vessel. The reaction is exothermic. The reaction product is washed with water to remove the excess acid and is then distilled.

Table 77 gives the physical properties of the compounds prepared by this method (Bibl. 58) (cf. p. 671).
### Table 76
Physical Properties of Thio-Esters of Orthosilicic Acid and of Chlorosilanes

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>a) Melting point</th>
<th>b) Boiling point</th>
<th>c) Specific gravity</th>
<th>d) Coefficient of expansion</th>
<th>e) Refractive index at</th>
<th>f) Library</th>
<th>g)</th>
<th>h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trichloromercaptosilane</td>
<td>Cl₂SiSH</td>
<td>95-97</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trichloro-(phenylthio)-silane</td>
<td>Cl₂SiSC₂H₅</td>
<td>110</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tri-((tert-butylthio)-chlorosilane)</td>
<td>(CH₃)₂CSiCl</td>
<td>71</td>
<td>161,3</td>
<td>(3-4 mm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetraethylthiosilane</td>
<td>(CH₂)₄Si₂</td>
<td>31</td>
<td>146 (12 mm)</td>
<td>1,0943</td>
<td>1,0860</td>
<td>1,0735</td>
<td>7,3</td>
<td>1,5687</td>
<td>1,5638</td>
</tr>
<tr>
<td>Tetra-(isopropylthio)-silane</td>
<td>(CH₂)₂CSi₂</td>
<td>-6</td>
<td>170 (12 mm)</td>
<td>1,0999</td>
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<td></td>
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<tr>
<td>Tetra-(propylthio)-silane</td>
<td>[((CH₃)₂CH₂)₂Si]</td>
<td>33,5</td>
<td>177 (14 mm)</td>
<td>1,0999</td>
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<tr>
<td>Tetra-(thiophene)-silane</td>
<td>(CH₃)₄Si₂</td>
<td>135,5</td>
<td>205 (17 mm)</td>
<td>1,0603</td>
<td>1,0328</td>
<td>1,0252</td>
<td>7,4</td>
<td>1,5468</td>
<td>1,5438</td>
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<tr>
<td>Tetrabutylthiosilane</td>
<td>(CH₂)₄CH₂CH₂Si₂</td>
<td>-</td>
<td>210 (4 mm)</td>
<td>1,0033</td>
<td>0,9968</td>
<td>0,9825</td>
<td>7,5</td>
<td>1,5336</td>
<td>1,5292</td>
</tr>
<tr>
<td>Tetra-(sec-butylthio)-silane</td>
<td>[((CH₂)₂CH₂)₂Si]</td>
<td>-</td>
<td>182 (4 mm)</td>
<td>1,0999</td>
<td>1,0022</td>
<td>0,9946</td>
<td>7,7</td>
<td>1,5396</td>
<td>1,5354</td>
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<tr>
<td>Tetra-(isobutylthio)-silane</td>
<td>((CH₂)₂CH₂CH₂Si₂</td>
<td>-</td>
<td>183 (4 mm)</td>
<td>0,9962</td>
<td>0,9326</td>
<td>0,9313</td>
<td>7,6</td>
<td>1,5298</td>
<td>1,5255</td>
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<tr>
<td>Tetra-(tert-butylthio)-silane</td>
<td>[((CH₃)₂CH₂)₂Si]</td>
<td>161</td>
<td>160-161</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Tetramethylthiosilane</td>
<td>(CH₃)₃H₂Si</td>
<td>-</td>
<td>231 (3,5 mm)</td>
<td>0,9810</td>
<td>0,9739</td>
<td>0,3666</td>
<td>7,5</td>
<td>1,5250</td>
<td>1,5212</td>
</tr>
<tr>
<td>Tetraacetylthiosilane</td>
<td>((CH₃)₂CH₂Si₂</td>
<td>50-51</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Tetra-cyclohexylthiosilane</td>
<td>(C₆H₁₂)₂Si₂</td>
<td>101,5-102,5</td>
<td></td>
<td></td>
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<tr>
<td>Tetraphenylthiosilane</td>
<td>(C₆H₁₂)₄Si₂</td>
<td>114,5-115</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Tetra-p-tert-butylphenylthiosilane</td>
<td>(C₆H₁₄)₄Si₂</td>
<td>185-186</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Tetra-(p-bromophenylthio)-silane</td>
<td>(Br₄)₄Si₂</td>
<td>216-218</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Tetra-(p-tolythio)-silane</td>
<td>((CH₃)₆Si₂</td>
<td>128,5-129</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Tri-(tert-butyl, mono)-methyldisilane</td>
<td>((CH₃)₂Si₂SiC₂H₅</td>
<td>43-44</td>
<td>159-60</td>
<td>(4 mm)</td>
<td></td>
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</tr>
<tr>
<td>Tri-(tert-butyln, mono)-methyldisilane</td>
<td>[((CH₃)₂Si₂SiC₂H₅</td>
<td>26-27</td>
<td>163,4</td>
<td>(4 mm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tri-(tert-butylthio)-isopropylthiosilane</td>
<td>[((CH₃)₂CSi₂SiC₂H₅</td>
<td>105</td>
<td>161-3</td>
<td>(3-4 mm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tris-(tert-butylthio)-hydroxysilane</td>
<td>[((CH₃)₂CSi₂SiOH]</td>
<td>90-91</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Name; (b) Formula; (c) Melting point; (d) Boiling point; (e) Specific gravity; (f) Coefficient of expansion; (g) Refractive index at; (h) Bibliography
Silicon Thioisocyanates

Organosilicon compounds containing the $-N=C=S$ group attached to the silicon atom, (which are called thioisocyanates), have long been known. Tetrathioisocyanatosilane was first prepared by reacting dry lead isothiocyanate with $SiCl_4$ (Bibl.59). Silicon thioisocyanates were later synthesized by the action of silver thiocyanate on alkyl- and arylchlorosilanes (Bibl.60). The thioisocyanatosilanes may be prepared by the following reactions:

$$SiCl_4 + 2(SCN)_2Pb \rightarrow Si(NCS)_4 + 2PbCl_2$$
$$RSiCl_4 + 3(SCN)Ag \rightarrow RSi(NCS)_4 + 3AgCl$$
$$R_2SiCl_4 + 2SCNAg \rightarrow R_2Si(NCS)_4 + 2AgCl$$
$$R_3SiCl + SCNAg \rightarrow R_3Si(NCS)_4 + Ag$$

where R is the radical $CH_3$, $C_6H_5$, etc.

Table 77

Physical Properties of Organothiosilanes (Bibl.58)

| Compound | a) $\text{CH}_3\text{Si}$(CH$_2$)$_n$SCH$_2$CONH$\text{C}_2$H$_5$ | b) $^\circ$C | c) $d_2^0$ | d) $n_D^0$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(Carboxymethylthioethy1)-trimethylsilane</td>
<td>(CH$_3$)$_3$Si(CH$_2$)$_n$SCH$_2$CONH$\text{C}_2$H$_5$</td>
<td>143–144 (7 mm)</td>
<td>1.0139</td>
<td>1.4811</td>
</tr>
<tr>
<td>(Carboxymethylthiopropyl)-trimethylsilane</td>
<td>(CH$_3$)$_3$Si(CH$_2$)$_n$SCH$_2$CONH$\text{C}_2$H$_5$</td>
<td>164–166 (9 mm)</td>
<td>1.0099</td>
<td>1.4790</td>
</tr>
<tr>
<td>(Carboxymethylthiopropyl)-pentamethyldisiloxane</td>
<td>(CH$_3$)$_3$Si–O–Si(CH$_3$)$_n$H$_2$–SCH$_2$COOH</td>
<td>149–150 (2 mm)</td>
<td>0.9902</td>
<td>1.4588</td>
</tr>
<tr>
<td>(Ethylcarboxymethylthiopropyl)-trioxysilane</td>
<td>(C$_2$H$_5$O)$_2$Si(CH$_2$)$_n$SCH$_2$COOCH$_3$</td>
<td>200–201 (50 mm)</td>
<td>1.0301</td>
<td>1.4479</td>
</tr>
<tr>
<td>(Ethylcarboxymethylthiopropyl)-trimethylsilane</td>
<td>(CH$_3$)$_3$Si(CH$_2$)$_n$SCH$_2$CONH$\text{C}_2$H$_5$</td>
<td>148–149 (24 mm)</td>
<td>0.9493</td>
<td>1.4630</td>
</tr>
<tr>
<td>(Tolythiopropyl)-trimethylsilane</td>
<td>(CH$_3$)$_3$Si(CH$_2$)$_n$Sc$_2$H$_5$H$_2$</td>
<td>206–209 (48 mm)</td>
<td>0.9408</td>
<td>1.5267</td>
</tr>
</tbody>
</table>

a) Formula; b) Boiling point, $^\circ$C; c) Specific gravity $d_2^0$; d) Refractive index $n_D^0$

The reaction between silver or lead thioisocyanate and $SiCl_4$, alkyl- or aryl-
Chlorosilanes lead is conducted in inert solvents: benzene, toluene, isopropylbenzene, etc.

**Preparation of Phenylthioisocyanatosilanes.** A 30% solution of 1 mol of phenyltrichlorosilane or other phenylchlorosilane is prepared, and the quantity of silver isothiocyanate calculated from the equation of the reaction is added to it in several portions. The mixture is heated for one hour, with stirring, at 80 - 90°C. The silver chloride is then filtered off and washed with benzene. The benzene is evaporated at atmospheric pressure, and the residue is vacuum distilled. The phenyltrithioisocyanatosilane is distilled under 3 mm pressure. The yield is 70 - 80% of theoretical.

The ethylthioisocyanatosilanes have been prepared from ethyltrichlorosilane and diethylchlorosilane. The presence of admixtures of ethyltribromosilane was of no consequence, since the thioisocyanato group replaces both chlorine and bromine attached to the silicon atom.

**Preparation of Ethylthioisocyanatosilane (Bibl.61).** A solution of 20 g of ethyltrichlorosilane in benzene, or a solution of diethylchlorosilane, is treated with silver isocyanate, taken in 30% excess over the theoretical quantity. After heating 30 min. at 85°C, followed by filtration, washing the precipitated silver halides with benzene, and evaporating the benzene, ethyltrithioisocyanatosilane or diethylthioisocyanatosilane, respectively, is obtained in yield of about 85% of theoretical.

**Physical Properties of Silicon Thioisocyanates**

All the phenylthioisocyanatosilanes, as well as the tetrathioisocyanatosilanes, are colorless crystalline substances. The phenylthioisocyanatosilanes tend to supercooling on crystallisation: diphenylthioisocyanatosilane, by 46°C, triphenylthioisocyanatosilane, by 20°C.

Table 78 gives the physical properties of the alkyl-(aryl)-thioisocyanato-
When ethyltrithioisocyanatosilane is cooled to -70°C, a very viscous liquid is obtained, which crystallizes only when stirred with a small quantity of ground glass.

Table 78

Physical Properties of Alkyl-(Aryl)-Thioisocyanatosilanes

<table>
<thead>
<tr>
<th></th>
<th>a)</th>
<th>b)</th>
<th>c) °C</th>
<th>d) °C</th>
<th>e) d^20</th>
<th>f) n^20_D</th>
<th>g)</th>
<th>h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tri-(thioisocyanato)-methylsilane</td>
<td>CH₂₅Si(CN₅)₃</td>
<td>-</td>
<td>266.8</td>
<td>1.394</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>68</td>
</tr>
<tr>
<td>Tri-thioisocyanatodimethylsilane</td>
<td>(CH₃)₂Si(CN₅)₂</td>
<td>-</td>
<td>217.3</td>
<td>1.142</td>
<td>1.5677</td>
<td>-</td>
<td>-</td>
<td>68</td>
</tr>
<tr>
<td>Tri-thioisocyanatoethylsilane</td>
<td>(CH₃)₃Si(CN₅)</td>
<td>-</td>
<td>143.1</td>
<td>1.134</td>
<td>1.4426</td>
<td>-</td>
<td>-</td>
<td>68</td>
</tr>
<tr>
<td>Tri-thioisocyanatotrimethylsilane</td>
<td>(C₃H₇)₃Si(CN₅)</td>
<td>-</td>
<td>210.5</td>
<td>0.934</td>
<td>0.4944</td>
<td>54.06</td>
<td>61.68</td>
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<tr>
<td>Tri-thioisocyanatodiphenylsilane</td>
<td>(C₆H₅)₂Si(CN₅)</td>
<td>-</td>
<td>245.5</td>
<td>1.089</td>
<td>1.5540</td>
<td>59.42</td>
<td>61.68</td>
<td></td>
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<tr>
<td>Tri-thioisocyanatodiphenylsilane</td>
<td>(C₆H₅)₂Si(CN₅)</td>
<td>-</td>
<td>276±2</td>
<td>1.264</td>
<td>1.6195</td>
<td>64.25</td>
<td>61.68</td>
<td></td>
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<tr>
<td>Tetrathioisocyanatosilane</td>
<td>Si(CN₅)₄</td>
<td>-</td>
<td>414.2</td>
<td>1.400</td>
<td>-</td>
<td>-</td>
<td>70.4</td>
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<tr>
<td>Tri-thioisocyanatopropylsilane</td>
<td>C₃H₇Si(CN₅)</td>
<td>-</td>
<td>152±151</td>
<td>1.2248</td>
<td>1.6014</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Tri-thioisocyanatopropylsilane</td>
<td>C₃H₇Si(CN₅)</td>
<td>-</td>
<td>137±138</td>
<td>1.2177</td>
<td>1.6066</td>
<td>-</td>
<td>-</td>
<td>68</td>
</tr>
<tr>
<td>Tri-thioisocyanatobutylsilane</td>
<td>C₄H₉Si(CN₅)</td>
<td>-</td>
<td>135±136</td>
<td>1.1811</td>
<td>1.5928</td>
<td>-</td>
<td>-</td>
<td>68</td>
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<tr>
<td>Tri-thioisocyanatophenylsilane</td>
<td>C₆H₅Si(CN₅)</td>
<td>-</td>
<td>135±136</td>
<td>1.1811</td>
<td>1.5928</td>
<td>-</td>
<td>-</td>
<td>68</td>
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<tr>
<td>Tri-thioisocyanatomethylsilane</td>
<td>C₅H₅Si(CN₅)</td>
<td>-</td>
<td>396</td>
<td>1.496</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Tri-thioisocyanatobenzylsilane</td>
<td>C₆H₅Si(CN₅)</td>
<td>-</td>
<td>46</td>
<td>1.188</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Tri-thioisocyanatobenzylsilane</td>
<td>C₆H₅Si(CN₅)</td>
<td>-</td>
<td>52</td>
<td>1.399</td>
<td>1.3291</td>
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<td>68</td>
</tr>
<tr>
<td>Thioisocyanatoisocyanato- methoxysilane</td>
<td>C₄H₅ClSi(CN₅)</td>
<td>-</td>
<td>171±172</td>
<td>1.2775</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>68</td>
</tr>
<tr>
<td>Thioisocyanatoisocyanato- methoxysilane</td>
<td>C₄H₅ClSi(CN₅)</td>
<td>-</td>
<td>170.5</td>
<td>1.34</td>
<td>1.4426</td>
<td>-</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>Thioisocyanatoisocyanato- methoxysilane</td>
<td>C₄H₅ClSi(CN₅)</td>
<td>-</td>
<td>122.2±122.6</td>
<td>1.036</td>
<td>1.4431</td>
<td>-</td>
<td>-</td>
<td>68</td>
</tr>
<tr>
<td>Thioisocyanatoisocyanato- methoxysilane</td>
<td>C₄H₅ClSi(CN₅)</td>
<td>-</td>
<td>129.5</td>
<td>-</td>
<td>1.461</td>
<td>-</td>
<td>-</td>
<td>68</td>
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<tr>
<td>Thioisocyanatoisocyanato- methoxysilane</td>
<td>C₄H₅ClSi(CN₅)</td>
<td>-</td>
<td>98</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>68</td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Melting Point, °C; d) Boiling point, °C; e) Specific gravity, d^20; f) Refractive index n^20_D; g) Molecular refraction; h) Bibliography

Triethylthioisocyanatosilane has the odor of camphor, melts at -30°C, and is slowly hydrolyzed at room temperature, or, somewhat more rapidly, at 80°C. Diethyldithio-
isocyanatosilane, ethyltrithioisocyanatosilane, and tetrathioisocyanatosilane are hydrolyzed at rates increasing in that order.

The thioisocyanatosilanes are soluble in benzene, \( \text{CCl}_4 \), benzine; methanol and ethanol readily dissolve trithioisocyanatosilane and dithioisocyanatodiphenylsilane, but thioisocyanatotriphenylsilane are sparingly soluble in them.

When the phenylthioisocyanatosilanes are dissolved in alcohols, partial decomposition is observed. Tetrathioisocyanatosilane does not dissolve in ether, and is decomposed in alcohols.

**Chemical Properties of Silicon Thioisocyanates**

Under the action of methanol on silicon tetrathioisocyanate, thioisocyanatotrimethoxysilane is formed (Bibl.62):

\[
3 \text{CH}_3\text{OH} + \text{Si(NCS)}_4 \rightarrow (\text{CH}_3\text{O})_3\text{SiNCS} + 4\text{HCNS}
\]

When aniline acts in the cold on a benzene solution of tetrathioisocyanatosilane, tetraphenylaminosilane (Bibl.63) and a double compound of thiocyanic acid with aniline are formed:

\[
\text{Si(NCS)}_4 + 4\text{C}_6\text{H}_5\text{NH}_2 \rightarrow \text{Si(NHC}_6\text{H}_5)_4 + 4\text{HNCS}
\]

Under the action of water, tetraisothiocyanatosilane decomposes:

\[
\text{Si(NCS)}_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{HCNS}
\]

Alkali accelerates this decomposition. In this case a salt of orthosilicic acid is formed:

\[
\text{Si(NCS)}_4 + 8\text{KOH} \rightarrow \text{Si(O)}_3\text{K} + 4\text{KNCS} + 4\text{H}_2\text{O}
\]

Aqueous ammonia decomposes tetrathioisocyanatosilane, and strong heating takes place. The behavior of the thioisocyanatophenylsilanes to the action of water dif-

?TS-9191/V 674
fers sharply from that of tetraethioisocyanatosilane; thus, for example, thioisocyanato
triphenylsilane is practically inert to the action of water, dithioisocyanatodiphenylsilane is hydrolyzed with difficulty, and only trithioisocyanatophenylsilane hydrolyzes readily. This shows that with increasing number of phenyl groups in the molecules of thioisocyanatophenylsilanes, the velocity of hydrolysis falls sharply.

**Silicon Compounds Containing Phosphorus, Selenium, Lead and other Elements**

Organosilicophosphorus compounds have been little studied. B. Arbuzov and A. Pu
lovin (Pitl.64) have studied the reaction between triethylbromosilane and triethyl phosphite, and between triethoxycchlorosilane and triethyl phosphite. They found that when triethylbromosilane acts on triethylphosphate, diethoxyphosphatotriethylsilane is obtained:

\[
(C_2H_5)_3SiBr + P(OC_2H_5)_3 \rightarrow (C_2H_5)_3Si-P(OC_2H_5)_2 + C_2H_5Br
\]

Under the action of triethoxycchlorosilane on triethyl phosphite, diethoxyphosphatotriethylsilane was formed:

\[
(C_2H_5)_3SiOC_2H_5 + P(OC_2H_5)_3 \rightarrow (C_2H_5)_3Si-P(OC_2H_5)_2 + C_2H_5Cl
\]

This reaction was accompanied by the formation of considerable quantities of tetraethoxysilane.

A study of the strength of the Si-P bond showed it to be weak. On heating to 200°C, diethoxyphosphatotriethoxysilane breaks down, with formation of tetraethoxysilane. Under the action of chlorine on this compound, cleavage takes place at room temperature:

\[
(C_2H_5)_3Si-P(OC_2H_5)_2 + Cl_2 \rightarrow (C_2H_5)_3SiCl + 2P(OC_2H_5)_3
\]

The bond between the silicon atom and the -OP group is also weak. This con-
Conclusion can be drawn from the following example. On hydrolysis of methylchloro-
trimethylsilane by water, an oily substance of molecular weight 110 is formed, which consists
of a mixture of polyethylharmoinsiloxanes. Heating of this oily substance with P_2O_5
(10%) at 200°C for 24 hours yields a solid product. Then a large quantity of P_2O_5 is
used, the oily substance is converted into a solid even at room temperature (Bibl.65).
In this case the reaction is accompanied by the liberation of heat, and a solid gela-
tious product is obtained. When the solid products are heated with water, they are
hydrolized and converted back into liquid oily substances. The molecular weights
given below for samples of these polyethylsiloxane oils before and after treatment with
phosphorus pentoxide, and after the subsequent hydrolysis by hot water, show that the
molecular weight of the product obtained after such treatment and hydrolysis varied
less than it ill on ordinarv heating of the oily product.

<table>
<thead>
<tr>
<th>Molecular weight of oil:</th>
<th>440</th>
<th>630</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before treatment</td>
<td></td>
<td></td>
</tr>
<tr>
<td>after 24-hour heating at 200°C, followed by hydrolysis</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Molecular weight of substance after
24-hour heating in the presence of various quantities of P_2O_5,
followed by hydrolysis:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Molecular weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>30% P_2O_5</td>
<td>580</td>
</tr>
<tr>
<td>10% P_2O_5</td>
<td></td>
</tr>
<tr>
<td>20% P_2O_5</td>
<td>450</td>
</tr>
</tbody>
</table>

Appearance of substance after adding P_2O_5 before heating

<table>
<thead>
<tr>
<th>Appearance of substance after adding P_2O_5 before heating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscous liquid</td>
</tr>
</tbody>
</table>

This may be explained by the following reaction of phosphorus pentoxide:

\[
\begin{align*}
\text{Si-O-P-O-Si} & \rightarrow 2\text{H}_2\text{O} + 2\text{SiO}_2 \\
2\text{SiO}(1) + \text{P}_2\text{O}_5 & \rightarrow 2\text{SiO} + 2\text{H}_2\text{O}
\end{align*}
\]
with the formation of a space polymer. The hydrolytic instability of the Si – O – P bond, however, leads to the decomposition of such polymer, liberating the oil and phosphoric acid. The direct reaction of condensation between the hydroxyl groups attached to the silicon atoms is under these conditions suppressed by the competing reaction of addition of phosphorus pentoxide. For this reason the molecular weight of the product varies less with increasing quantity of phosphorus pentoxide than it does in the control sample.

Preparation of diethoxyphosphatetriethylsilane. A mixture of 10 g of triethylbromosilane and 8.3 g of triethyl phosphite is heated in a Wurtz flask on the water bath. The reaction begins at 70°C, and the ethyl bromide is distilled off at the same time. After this removal has been completed, the reaction product is separated by vacuum distillation; boiling point 158 – 159°C (10 mm); specific gravity $d_4^{20} = 0.9659$; refractive index 1.4390.

Diethoxyphosphatetriethoxysilane, prepared similarly, boils at 113°C (12 mm). Its specific gravity $d_4^{20} = 0.9282$ and its refractive index is 1.4080.

Silicon compounds containing selenium are also known (Bibl.66). When selenophenols react with SiCl$_4$ in benzene solution, tetraphenylselenosilane is formed:

$$4C_6H_5SeH + SiCl_4 \rightarrow 4HCl + Si(SeC_6H_5)_4$$

This reaction takes place only for selenophenol. Other compounds of analogous type have been prepared by the action of metallic sodium on a mixture of selenophenol and SiCl$_4$.

When a polyorganosiloxane liquid is heated in the presence of lead, it gradually becomes turbid, and toward the end of the heating a precipitate accumulates on the bottom of the reaction flask.

Patnode and Schmidt (Bibl.67) postulate that lead oxide can react with polysiloxanes by Formula I. They consider this hypothesis to be proved by the reaction between trimethylsilanol and lead oxide, (Formula II), which they have investigated:
The turbidity in the liquid during the process of heating in the presence of lead might be due to the formation of plumboxysilanes. These lead compounds are thermally unstable, and, on heating, might yield products of low molecular weight, which would evaporate. The increased losses with rising temperature indicate that the reaction of the breakdown of the plumboxysilanes becomes more intense with rising temperature.

Preparation of Bis-trimethylplumboxysilane. About 1 g of lead oxide is shaken with 25 ml of trimethylsilanol at room temperature for 2 days. The yellow color of the lead oxide gradually changes to white. Filtration of the mixture and evaporation of the liquid yields a white crystalline substance, soluble in ether, toluene and absolute ethanol. It has the composition (CH₃)₃SiOPbOSi(CH₃)₃, but the calculated lead content, 53.7%, differs greatly from the content found, 59.1%. The analysis is made by precipitating the lead by dilute sulfuric acid from an alcoholic solution of a weighed portion of bis-trimethylplumboxysilane.

Organic silicon compounds containing other elements in the molecule (lead, tin, arsenic, mercury, etc.) have as yet been synthesized only in small numbers.

Table 79 gives the physical and chemical properties of certain representatives of these compounds.
Table 79

Physical Properties of Organic Silicon Compounds Containing Lead, Tin, Arsenic and Mercury (Bibl.68)

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c) °C</th>
<th>d) °C</th>
<th>e) d₄</th>
<th>f) n°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trimethyllead-(phenylene)-triethylsilane</td>
<td>(C₆H₅)₃SiC₆H₄Pb(CH₃)₃</td>
<td>191 (17 mm)</td>
<td>—</td>
<td>1.3997 (24°)</td>
<td>1.54937</td>
</tr>
<tr>
<td>Triethyltin-(phenylene)-triethylsilane</td>
<td>(C₆H₅)₃SiC₆H₄Sn(C₆H₅)₃</td>
<td>214 (18 mm)</td>
<td>—</td>
<td>1.1216 (21.2°)</td>
<td>1.52756</td>
</tr>
<tr>
<td>Diphenylarsine-(phenylene)-triethylsilane</td>
<td>(C₆H₅)₂SiC₆H₄A-(C₆H₅)₃</td>
<td>279—81 (17 mm)</td>
<td>—</td>
<td>1.1661 (21.3°)</td>
<td>1.61455</td>
</tr>
<tr>
<td>Mercurochloromethyltrimethylsilane</td>
<td>CH₃CH(H₂Cl)Si(CH₃)₃</td>
<td>—</td>
<td>97</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Mercurochloromethyltrimethylsilane</td>
<td>(CH₃)₃SiCH₃HgCl</td>
<td>—</td>
<td>74—6</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Double Compounds:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diphenylarsine-(phenylene)-triethylsilane with mercuric chloride</td>
<td>(C₆H₅)₂A-(C₆H₅)₃Si(C₆H₅)₂.HgCl₂</td>
<td>—</td>
<td>188</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Same, with mercuric bromide</td>
<td>(C₆H₅)₂A-(C₆H₅)₃Si(C₆H₅)₂.HgBr₂</td>
<td>—</td>
<td>181</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Same, with mercuric iodide</td>
<td>(C₆H₅)₂A-(C₆H₅)₃Si(C₆H₅)₂.HgI₂</td>
<td>—</td>
<td>139.5</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

a) Name; b) Formula; c) Boiling Point; d) Melting point; e) Specific gravity; f) Refractive index
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CHAPTER IX

LOW-MOLECULAR ORGANO SILICON POLYMERS

In our discussion of the processes of hydrolysis of the halosilanes and alkoxy-
silanes, we have already described certain low-molecular siloxanes.

In the present Chapter we shall consider only polymers with alternating silicon
and carbon atoms in the chain, as well as polysiloxanes containing chloromethyl and
certain other groups.

Compounds with Alternating Atoms of Silicon and Carbon

The thermal and hydrolytic stability of the methyl groups attached to the sili-
con atom led investigators to the conclusion that compounds containing a chain of
molecules of alternating atoms of silicon and carbon should likewise be stable. Such
compounds prove to be interesting as well by reason of the fact that, unlike the
polyorganosiloxanes, they do not undergo thermal or catalytic rearrangement.

The study of the compounds containing the \(-\text{Si} - \text{C} - \text{Si}\)- bond in the chain

has commenced only recently, and the data in the literature on this subject are very
limited. Such compounds have been prepared by the action of a mixture of various
quantities of methylene dichloride and nitrogen on an alloy of copper and silicon
at 300-400°C. This gives a product mixture, from which pentachloromethylenedisilane
and hexachloromethylenedisilane have been isolated (Bibl.1). When a mixture of di-
chloromethane and nitrogen is passed over a copper-silicon alloy at 300°C, cyclic
compounds containing the methylene group attached to two silicon atoms are formed. In
this case hexachlorocyclotri(methylene) silane was obtained.

In collaboration with M.D. Frenkel, I have prepared hexachloroethylenedisilane
by passing dichlorethane over a copper-silicon alloy at 280°C.
A number of compounds containing the grouping \(-\text{Si} - \text{CH}_2 - \text{Si}\) in the molecule have been synthesized by the Grignard reaction (Bibl.2) followed by treatment of the reaction product with sulfuric acid and HF:

\[
\begin{align*}
(\text{CH}_3)_2\text{SiOSi(CH}_3)_2\text{CH}_2\text{MgCl} & + (\text{CH}_3)_2\text{SiCl}_2 \rightarrow \text{(CH}_3)_2\text{SiOSi(CH}_3)_2\text{CH}_2\text{Cl}
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{O} & \\
\rightarrow & \text{(CH}_3)_2\text{SiOSi(CH}_3)_2\text{SiCl}_2
\end{align*}
\]

\[
\begin{align*}
\text{HF} & + \text{H}_2\text{SO}_4
\end{align*}
\]

\[
\begin{align*}
\text{FSi(CH}_3)_2\text{CH}_2\text{Si(TH}_3)_2\text{F} & + (\text{CH}_3)_2\text{SiF} + \text{H}_2\text{O}
\end{align*}
\]

Preparation of difluorotetramethylmethylenedisilane. In a 3 liter flask 126 g of magnesium, 200 ml of dried ethyl ether, and a small crystal of iodine are placed, and a solution of 1080 ml (5 mols) of pentamethylchloromethylidisiloxane (boiling point 151-152°C) in 1 liter of dried ether is added. The formation of the organomagnesium compound is slow at first. The reaction is accelerated by adding a few drops of ethyl iodide to the mixture. The addition of the pentamethylchloromethyl-disiloxane takes about 6 hours, after which the mixture is held a few hours longer at the boiling point.

The Grignard reagent so prepared reacts rapidly with dimethyldichlorosilane. The reagent prepared from 5 mols of pentamethylchloromethylidisiloxane is added to a solution of 665 ml (5.5 mols) of dimethyldichlorosilane in 800 ml of dried ether over a period of 2 hours. A certain amount of heat is given off during this addition. When the addition of the Grignard reagent has been completed, the reaction mass is heated for 15 minutes. The reaction product is then poured onto ice, and the ethereal layer is separated, washed, and dried over sodium sulfate. The ether is then distilled off, yielding 1130 g of an oily substance, which is added, with stirring, to 1100 ml of strong sulfuric acid. During this addition, a certain amount of HCl is evolved, probably owing to the continuing hydrolysis of the incompletely hydrolyzed high-molecular chlorosilanes. The maximum temperature during the addition is 68°C. The cooled solution of the oily substance in the sulfuric acid is placed in
a flask and a stream of anhydrous HF is passed in and bubbled directly through the solution for 2 hours. The HF is rapidly absorbed, and gaseous trimethylfluorosilane is given off at the same time. Soon after the passage of the HF is commenced, an upper layer containing the organosilicon compounds begins to separate. When the absorption of the HF has been completed, this upper layer is rapidly removed and fractionated. A fraction in the boiling range 114-116°C, amounting to 532 g, is collected. This consists of difluorotetramethylmethylenedisilane.

If 2 mols of organomagnesium compound for each mol of dimethyldichlorosilane is taken, then, when the reaction is conducted similarly, compounds with mixed siloxane-silicocarbon chains are formed.

To a Grignard reagent, prepared as described above from 2.5 mols of pentamethyldichlorodisiloxane in 550 ml of dry ether, 145 ml (1.2 mol) of dimethyldichlorosilane is added over the course of 30 min. The mixture is then heated to boiling for 2.5 hours. The reaction product is poured on ice, and the ethereal layer is separated, washed, and dried over sodium sulfate. The ether is distilled off, together with the hexamethyldisiloxane formed as a by product. The oily residue is slowly distilled at 50°C up to 235°C, and the distillate so obtained is fractionated. The fraction boiling in the range of 99-101°C (57 mm) is a compound of the structure

$$(\text{CH}_3)_2\text{SiOSi(\text{Cl}_3)}_2\text{CH}_3\text{Si(\text{CH}_3)}_2$$

while the fraction boiling in the range 175-177°C (55 mm) is

$$(\text{CH}_3)_2\text{SiOSi(\text{Cl}_3)}_2\text{CH}_3\text{Si(\text{CH}_3)}_2\text{CH}_2\text{Si(\text{CH}_3)}_2\text{OSi(\text{CH}_3)}_2$$

The yields of these fractions are respectively 7.22 and 10% of the weight of the oily substance taken for distillation. The high-boiling residue (159 g) which is not distilled in vacuo, is dissolved in 160 ml of conc. sulfuric acid and treated with HF as described above. On distillation of the reaction product only 99 g of
liquid, boiling point 114-115°C is obtained. This fraction consists of difluoro-
tetramethylmethylenedisilane, \( \text{F}(\text{CH}_3)_2 \text{SiCH}_2 \text{Si}(\text{CH}_3)_2 \text{F} \). The yield is 48 % of theoretical.

Difluorotetramethylmethylenedisilane has a pleasant odor recalling that of the
silanols. It is slowly hydrolyzed, and may be kept in a closed glass vessel, in
which only insignificant signs of the etching of the glass are observed. On the hy-
drolysis of this compound in an alkaline medium, tetramethylmethylenedisilanediol is
formed; when the hydrolysis is conducted with heating or in an acid medium, an oily
substance is separated.

Hydrolysis of difluorotetramethylmethylenedisilane. Under cooling, 15 g of
tetramethyldifluoromethylenedisilane is shaken with an excess of dilute alkali solu-
tion, forming two layers, a solid and a liquid. The solid layer is filtered off,
yielding 7 g of white needles, which, after recrystallization from benzene, have
the melting point 84-86°C, and are, \( \text{HO} \text{Si}(\text{CH}_3)_2 \text{CH}_2 \text{Si}(\text{CH}_3)_2 \text{OH} \), tetramethylmethylenedi-
silanediol. This product is soluble in acetone and \( \text{CCl}_4 \). It is also somewhat soluble
in water. When heated to a temperature somewhat above the melting point, or when an
aqueous solution is acidified, it is converted into a polymeric oil. Difluorotetra-
methylmethylenedisilane may also be hydrolyzed by heating. For this purpose, 1.3
mols of the product is boiled 3 hours with a solution of 3 mols of KOH in 1 liter of
water. The oil separated is washed with a saturated solution of NaCl and then with
water. The washed oil is shaken with 10 ml of conc. sulfuric acid and then washed
again with water. After drying over calcined potassium carbonate and filtration, the
filtered oil is of the following composition.

\[ (\text{CH}_3)_2 \text{SiCH}_2 \text{Si}(\text{CH}_3)_2 \text{Cl}_n \]

Vacuum distillation of the oil yields a cyclic product of boiling point 103-104°C
(20 mm) and melting point 28-29°C, of the composition:
The chlorine derivatives may be prepared from the difluoride by the reaction:

\[
\text{FSi(CH}_3\text{)}_2\text{CH}_3\text{Si}(\text{CH}_3\text{)}_2\text{F} + \text{Si(CH}_3\text{)}_2\text{Cl} \xrightarrow{\text{AlCl}_3} \text{FSi(CH}_3\text{)}_2\text{CH}_3\text{Si}(\text{CH}_3\text{)}_2\text{Cl} + \text{ClSi(Ch}_3\text{)}_2\text{Si(Ch}_3\text{)}_2\text{Cl} + (\text{CH}_3\text{)}_2\text{SiF}
\]

Preparation of dichlorotetramethylmethylenedisilane. A solution of 0.2 mol of difluorotetramethylmethylenedisilane and 0.5 mol trimethylchlorosilane is boiled 3 hours. During the boiling of the mixture traces of trimethylfluorosilane are driven off and caught in a trap chilled by solid carbon dioxide. The reaction does not proceed without the addition of aluminum chloride. After adding 1 g of aluminum chloride and heating the mixture to the boiling point of trimethylchlorosilane, an appreciable quantity of trimethylfluorosilane suddenly begins to condense in the trap. The trimethylchlorosilane driven off is returned to the reaction flask in small portions. The reaction temperature is held at about 30°C. Fractionation of the reaction mixture under reduced pressure yields two fractions with the respective boiling ranges of 71-72°C (50 mm) and 95-96°C (50 mm). The first fraction is fluorochlorotetramethylmethylenedisilane, FSi(CH_3)_2CH_2Si(CH_3)_2Cl in 26% yield, while the latter fraction is dichlorotetramethylmethylenedisilane, ClSi(CH_3)_2CH_2Si(CH_3)_2Cl, in 47% yield. The mixed chlorofluorotetramethylmethylenedisilane undergoes a disproportionation reaction already during the process of distillation under atmospheric pressure.

The methylene groups between the silicon atoms are bound rather firmly to the silicon. Concentrated sulfuric acid, HF, and a boiling alkali solution all fail to break this bond; but it is sensitive to the action of the atmospheric oxygen at elevated temperatures. One of its oxidation products is formaldehyde. In the absence of oxygen, such compounds are thermally stable.

Compounds with alternating silicon and carbon atoms in the molecular chain
may also be prepared by the action of lithium (Bibl.3)

Chloromethyltrimethylsilane reacts with lithium to form lithiummethyltrimethylsilane. These organometallic compounds have been used by various investigators in the synthesis of alkyl-substituted silanes:

\[
2(\text{CH}_3)\text{SiCH}_2\text{Li} + (\text{CH}_3)\text{SiCl}_2 = (\text{CH}_3)\text{SiCH}_2\text{Si}((\text{CH}_3)_2\text{CH})_2 + 2\text{LiCl}
\]

\[
(\text{CH}_3)\text{SiCH}_2\text{Li} + \text{ClSi(\text{CH}_3)_2\text{Cl}} = (\text{CH}_3)\text{SiCH}_2\text{Si}((\text{CH}_3)_2\text{CH})_2 + \text{LiCl}
\]

\[
2(\text{CH}_3)\text{SiCH}_2\text{Li} + (\text{CH}_3)\text{SiCl}_2 = (\text{CH}_3)\text{SiCH}_2\text{Si}((\text{CH}_3)_2\text{CH})_2 + 2\text{LiCl}
\]

When 0.155 mol of dimethyldichlorosilane is poured over a period of 4.5 min. into 0.5 mol of \((\text{CH}_3)_3\text{SiCH}_2\text{Li}\), diluted with 500 cm\(^3\) of pentane, and the mixture is heated 12 hours, after which the pentane is distilled off, octamethyldimethylenetrilane \(\text{CH}_3[(\text{CH}_3)_3\text{SiCH}_2]_2\text{Si}(\text{CH}_3)_2\), decamethyldimethylenetetrasilane, \(\text{CH}_3[(\text{CH}_3)_3\text{SiCH}_2]_2\text{Si}(\text{CH}_3)_3\), and dodecamethyltetramethylenepentasilane, \(3\text{CH}_33\text{SiCH}_23\text{Si}(\text{CH}_3)_3\), are formed.

Preparation of polyalkylmethylenehalosilanes (Bibl.3). 1. After 7 hours of heating at 375°C, under pressure of 50-70 atm, of a mixture of 885 parts of \((\text{CH}_3)_3\text{SiCl}\) and 23 parts of \(\text{AlCl}_3\), a certain quantity of \(\text{CH}_2[\text{Si}(\text{CH}_3)_2\text{Cl}]_2\) is formed; boiling point 176-177°C (75\(^\circ\) mm); refractive index \(nD^20 = 1.016\).

A solution of 179 g of \(\text{ClCH}_2\text{Si}(\text{CH}_3)_2\text{OOSi}(\text{CH}_3)_3\) in 300 g of ether is poured over a period of 2 hours, into a mixture of 23 g of magnesium and 50 g of ether. The mixture is then heated 0.5 hour, and a solution of 2.2 ml of \((\text{CH}_3)_2\text{SiCl}_2\) in ether is added to the Grignard reagent so formed. The mixture is heated 1.5 hour, and is then hydrolyzed 0.25 hour by ice water, yielding 200 g of \((\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_2\text{CH}_2\text{Si}(\text{CH}_3)_3\) in the form of an oil, of which 100 g is now mixed with 500 ml of cold sulfuric acid and 117 g of \(\text{CaF}_2\). The product so prepared is extracted with pentane, giving 43 g of \(\text{CH}_2[\text{Si}(\text{CH}_3)_2\text{F}]_2\); b.p. 114-116°C; specific gravity \(d^20 = 0.920\); refractive index \(nD^20 = 1.3780\).

Preparation of polyalkylethylenehalosilanes. To 11.0 g of lithium foil, in 1000 ml
of boiling pentane, period of 2 hours, 125 g of trimethylchloromethyilsilane is added. The pentane is then gradually distilled off over a 10-hour period. The yield of (CH$_3$)$_3$SiCH$_2$Li is about 86% of theoretical. When 0.86 mol of trimethylmethylthium-silane in 1 liter of pentane is heated 8 hours with 0.8 mol of dimethyldi-(chloromethyl)-silane, CICH$_2$Si(CH$_3$)$_2$CH$_2$Cl, chloromethylpentamethylethylenebisilane in 81% yield is obtained. On heating 12 hours, 1-chloromethylhexamethyldiethylenetri silane is formed. On heating 48 hours, 2-chloromethylnonamethyltri ethylenetetrasilane in 67% yield is obtained.

Heating a solution of (CH$_3$)$_3$SiCH$_2$MgCl with (CH$_3$)$_3$SiCH$_2$Cl in amyl ether to 130°C gives hexamethylethylenebisilane, (CH$_3$)$_3$SiCH$_2$CH$_2$Si(CH$_3$)$_3$. The yield is 40% of theoretical.

The polymethylmethylenesilanes may also be prepared by the condensation of chloromethyltrimethylchlorosilane with sodium in toluene. The reaction takes the following course:

$$nCICH$_2$Si(CH$_3$)$_2$Cl + 2nNa \rightarrow (CH$_3$)$_3$SiCH$_2$CH$_2$Si(CH$_3$)$_n + 2nNaCl$$

In this case the polymeric product [(CH$_2$Si(CH$_3$)$_2$)$_n$ is formed, where $n = 55$. A product with such a degree of polymerization is soluble only partially in hydrocarbons. In the presence of trimethylchlorosilane, the growth of the polymer chain is stopped.

On comparing the physical properties of polymers with alternating silicon and carbon atoms (cf. Table) with the literature data for the polydimethylsiloxanes, it will be noted that the elevation of the boiling point for each (CH$_3$)$_2$SiCH$_2$ group is greater than it is for each (CH$_3$)$_2$SiO group.

The variation in the viscosity of polymers with alternating silicon and carbon atoms with the temperature is more pronounced than in the case of polydimethylsiloxanes. The homologs studied have a higher heat of evaporation than the corresponding polydimethylsiloxanes. All these data compel the inference that the associative intermolecular forces are more pronounced in polymers with alternating silicon and
uni carbon atoms than in polydimethylsiloxanes.

Table 80 gives the physical properties of compounds with alternating silicon and carbon atoms in the chain (cf. p. 692).

LOW-MOLECULAR ORGANO SILICXANES

The literature describes a large number of low-molecular organosiloxanes, containing both like and unlike radicals. The disiloxanes have been studied in the greatest detail. Linear and cyclical polysiloxanes containing 10 and more silicon atoms in the molecule have also been isolated and characterized.

The methods of preparing them reduce down to the hydrolysis or cohydrolysis of the corresponding monomeric compounds, or to the thermal and catalytic rearrangement of disiloxanes and cyclic polymers. These methods have already been discussed in detail in Chapters IV, V and VI.

Hydrolysis of triethylchlorosilane by water leads to the formation of hexaethyl-disiloxane (Bibl. 4, 5, 6). On hydrolysis in an acid medium, of trialkylchlorosilanes containing mixed organic radicals attached to the same silicon atom, organosiloxanes are also formed. Thus, for example, tetramethyldiethyldisiloxane is formed from dimethylethylchlorosilane (Bibl. 7). Trimethyltriethyldisiloxane could be isolated by the combined hydrolysis of trimethylchlorosilane and triethylchlorosilane in an acid medium (Bibl. 8). On hydrolysis of triphenylchlorosilane, tribenzylchlorosilane and trixylylchlorosilane in an acid medium, hexaphenyldisiloxane, (Bibl. 9), hexa-xyldisiloxane (Bibl. 10), and hexaxylyldisiloxane (Bibl. 11) are formed, respectively. On the hydrolysis of alkyl-aryl-halosilanes, for instance, of methyl-phenylchloro silane, tetraphenylsiloxane is formed (Bibl. 12), while tetraphenyl-diethyldisiloxane is obtained as a result of the hydrolysis of diphenylethylchlorosilane (Bibl. 13). Diethylphenylchlorosilane is hydrolyzed in an acid medium, forming tetraethyl-diphenylsiloxane (Bibl. 14). Tetraphenyltrimethylsiloxane is formed by the hydrolysis of dibenzylmethylchlorosilane (Bibl. 15), while tetratenzyl-

F-7S-9121/V 691
<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexamethylmethyleneasilane</td>
<td>((\text{CH}_3)_3\text{Si(CH}_3\text{Si(\text{CH}_3)})</td>
</tr>
<tr>
<td>Octamethyltrimethylenetetrasilane</td>
<td>((\text{CH}_3)_4\text{Si(CH}_3\text{Si(\text{CH}_3)})</td>
</tr>
<tr>
<td>Decamethyltrimethylenetetrasilane</td>
<td>((\text{CH}_3)_5\text{Si(CH}_3\text{Si(\text{CH}_3)})</td>
</tr>
<tr>
<td>Dodecamethyltetramethylenepentasilane</td>
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<td>Chloromethylpentamethylenedisilane</td>
<td>((\text{CH}_3)_5\text{Si(CH}_3\text{Si(\text{CH}_3)})</td>
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<td>Chloromethylheptamethyldimethylenedisilane</td>
<td>((\text{CH}_3)_7\text{Si(CH}_3\text{Si(\text{CH}_3)})</td>
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<td>Dichlorotetramethylenedisilane</td>
<td>((\text{CH}_3)_3\text{Si(CH}_3\text{Si(\text{CH}_3)})</td>
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<td>Di-fluorotetramethylenedisilane</td>
<td>((\text{CH}_3)_3\text{Si(CH}_3\text{Si(\text{CH}_3)})</td>
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<td>Tetramethyltrifluoromethylenetrasilane</td>
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<td>Tetramethylfluorochloromethylenedisilane</td>
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<td>Hexachlorocyclotrimethylenetrasilane</td>
<td>((\text{CH}_3)_6\text{Si(CH}_3\text{Si(\text{CH}_3)})</td>
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<td>((\text{CH}_3)_5\text{Si(CH}_3\text{Si(\text{CH}_3)})</td>
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<td>Pentamethyl(diisoxamethylenemethyl)disilane</td>
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<td>((\text{CH}_3)_5\text{Si(OSi(\text{CH}_3)})</td>
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<td>Di-1,2-(methylenepentamethyldisiloxane)-tetramethyldisiloxane</td>
<td>((\text{CH}_3)_5\text{Si(OSi(\text{CH}_3)})</td>
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<td>1,2-Tetramethylenecyclohexadiisiloxane</td>
<td>((\text{CH}_3)_5\text{Si(OSi(\text{CH}_3)})</td>
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<tr>
<td>Di-1,2-(methylenepentamethyldisiloxane)-tetramethyldisiloxane</td>
<td>((\text{CH}_3)_5\text{Si(OSi(\text{CH}_3)})</td>
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(Cont'd. on p.692b)
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<th>Boiling Point</th>
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<td></td>
<td>at 780 mm</td>
<td>at 200 mm</td>
<td>at 20°C</td>
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<td>134</td>
<td>91</td>
<td>0.7520</td>
<td>1.4172</td>
</tr>
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<td>206</td>
<td>159</td>
<td>0.7987</td>
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<td>259</td>
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<td>1.4640</td>
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<td>141</td>
<td>0.8950</td>
<td>1.4480</td>
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<td>246</td>
<td>197</td>
<td>0.9000</td>
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<td>297</td>
<td>242</td>
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<td>—</td>
<td>95—96 (50 mm)</td>
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<tr>
<td>114—116</td>
<td>—</td>
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<td>—</td>
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<tr>
<td>187—188</td>
<td>102—102.5 (44 mm)</td>
<td>—</td>
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<td>—</td>
<td>71—72 (50 mm)</td>
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<tr>
<td>M. P. 84—86°C</td>
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<tr>
<td>M. P. 81—82°C</td>
<td>120—137 (10 mm)</td>
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<td>—</td>
<td>51 (10 mm)</td>
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<td>—</td>
<td>63.7 (10 mm)</td>
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<td>—</td>
<td>92.5 (25 mm)</td>
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<td>91—101 (55 mm)</td>
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<td>132—133 (55 mm)</td>
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<tr>
<td>173—177 (55 mm)</td>
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<tr>
<td>173—185 (34 mm)</td>
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<tr>
<td>173—184 (20 mm)</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>145 (2 mm)</td>
<td>— 0.8601</td>
<td>1.4542</td>
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<td>a)</td>
<td>b)</td>
<td>c) °C</td>
<td>d) °C</td>
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<tr>
<td>--------------------------</td>
<td>---------------------------</td>
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<tr>
<td>Hexamethyldisiloxane</td>
<td>(CH₃)₂SiOSi(CH₃)₂</td>
<td>100.4</td>
<td>107.3</td>
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<tr>
<td>Hexaethylsiloxane</td>
<td>(C₃H₇)₂SiOSi(C₃H₇)₂</td>
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<td>233</td>
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<td></td>
<td></td>
<td>129</td>
<td>117</td>
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<td>Hexaallyldisiloxane</td>
<td>(C₄H₉)₂SiOSi(C₄H₉)₂</td>
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<td>Hexabutyldisiloxane</td>
<td>(C₅H₁₁)₂SiOSi(C₅H₁₁)₂</td>
<td></td>
<td>138–140 (0.75 mm)</td>
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<tr>
<td>Hexamethylsiloxane</td>
<td>(C₆H₁₃)₂SiOSi(C₆H₁₃)₂</td>
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<td>360–370</td>
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<td>Hexabenzylsiloxane</td>
<td>(C₆H₅CH₂)₂SiOSi(C₆H₅CH₂)₂</td>
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<td>Hexatolyldisiloxane</td>
<td>(CH₃C₆H₄)₂SiOSi(CH₃C₆H₄)₂</td>
<td>223–224</td>
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<tr>
<td>Hexaethyldifosiloxane</td>
<td>(CH₃C₆H₄)₂SiOSi(CH₃C₆H₄)₂</td>
<td>19–20</td>
<td></td>
</tr>
<tr>
<td>Tetramethyl-1,2-disiloxane</td>
<td>(CH₃)₂C₆H₄SiOSi(CH₃)₂</td>
<td>150.5</td>
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<td>1,1-Dimethyl-2-triethylsiloxane</td>
<td>(CH₃)₂SiOSi(CH₃)₂</td>
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<tr>
<td>1,2-Dimethyltetrabiphenylsiloxane</td>
<td>(C₆H₅CH₂)₂SiOSi(C₆H₅CH₂)₂</td>
<td>51–52</td>
<td>51–52</td>
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<tr>
<td>1,2-Diethyltetraphenylsiloxane</td>
<td>(C₆H₅CH₂)₂SiOSi(C₆H₅CH₂)₂</td>
<td>65.4</td>
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<td>Tetraethyl-1,2-disiloxane</td>
<td>[CH₃C₆H₈CH₂]₂SiO²</td>
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<tr>
<td>1,2-Diethyltetrabenzylsiloxane</td>
<td>[CH₃C₆H₈CH₂]₂SiO²</td>
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<tr>
<td>1,2-Diethyltetrabenzylsiloxane</td>
<td>[CH₃C₆H₈CH₂]₂SiO²</td>
<td>227 (50 mm)</td>
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<tr>
<td>1,2-Di[(ethyl)(propyl) (benzyl)]-siloxane</td>
<td>[CH₃C₆H₈CH₂]₂SiO²</td>
<td>250–252 (25 mm)</td>
<td>250–252</td>
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<tr>
<td>1,2-Di[(butyl)(benzyl)]-</td>
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<td></td>
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<tr>
<td>siloxane</td>
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<td>1,1-allyldimethyl-2-triethyl-siloxane</td>
<td>CH₃ == CH–CH₂SiOSi(CH₃)₂</td>
<td>141.5</td>
<td>141.5</td>
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<tr>
<td>1,2-Diallyltetramethylsiloxane</td>
<td>CH₃ == CH–CH₂SiOSi(CH₃)₂</td>
<td>179–180 (75 mm)</td>
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<td>1,2-Diallyltetramethylsiloxane</td>
<td>CH₂Si(OSi(CH₃)₂Cl</td>
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<tr>
<td>1,2-Diallyltetramethylsiloxane</td>
<td>CH₂Si(OSi(CH₃)₂Cl</td>
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<td>Tetraethyl-1,2-dichlorosiloxane</td>
<td>(CH₃)₂SiOSi(CH₃)₂Cl</td>
<td>250–252 (25 mm)</td>
<td>250–252</td>
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<tr>
<td>Heptamethyltrisiloxane</td>
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a) Name; b) Formula; c) Melting point; d) Boiling point; e) Specific gravity; f) Refractive index; g) Bibliography
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<th>a)</th>
<th>b)</th>
<th>c) °C</th>
<th>d) °C</th>
<th>e) δ^4</th>
<th>f) δ^20</th>
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<td>Hexamethylcyclotrisiloxane</td>
<td>(CH₃)₃SiO₃</td>
<td>64–64.5</td>
<td>133–134</td>
<td>1.12 (solid)</td>
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<td>Hexaphenylcyclotrisiloxane</td>
<td>(C₆H₅)₃SiO₃</td>
<td>188</td>
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<td>–</td>
<td>–</td>
<td>22.24</td>
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<tr>
<td>Octamethyltrisiloxane</td>
<td>CH₃(CH₂)₃SiO₂</td>
<td>–80</td>
<td>153</td>
<td>0.9200</td>
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<tr>
<td>Triethyltrimethylcyclotrisiloxane</td>
<td>[CH₃]₃SiO₂</td>
<td>98</td>
<td>300–315 (22 mm)</td>
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<tr>
<td>Hexamethyl-1,3-dichlorotrisiloxane</td>
<td>[CH₃]₃SiO₂Cl</td>
<td>–53</td>
<td>184</td>
<td>1.018</td>
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<td>Tetrastiloxane</td>
<td>[CH₂]₄SiO₄</td>
<td>–69</td>
<td>134.5 (765 mm)</td>
<td>0.9938</td>
<td>1.3890</td>
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<td>Octamethylcyclotetrasiloxane</td>
<td>(CH₃)₄SiO₄</td>
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<td>175</td>
<td>0.9558</td>
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<td>Octamethyltetrasiloxane</td>
<td>(CH₃)₄SiO₄</td>
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<td>74 (20 mm)</td>
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<td>(CH₃)₅SiO₄</td>
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<td>194</td>
<td>0.8736</td>
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<td>Octamethyl-1,4-dichlorotetrasiloxane</td>
<td>(CH₃)₅SiO₄Cl</td>
<td>–80</td>
<td>222</td>
<td>1.011</td>
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<td>Pentamethylpentasiloxane</td>
<td>(CH₃)₅SiO₅</td>
<td>–106 ± 5</td>
<td>108.6 (755 mm)</td>
<td>1.0040</td>
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<td>85.6 (10 mm)</td>
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<td>Decamethylpentasiloxane</td>
<td>(CH₃)₆SiO₅</td>
<td>38–44</td>
<td>210</td>
<td>0.9593</td>
<td>1.3962</td>
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<td>Lodecamethylpentasiloxane</td>
<td>(CH₃)₆SiO₅</td>
<td>–80</td>
<td>101 (20 mm)</td>
<td>0.8755</td>
<td>1.3948</td>
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<tr>
<td>Hexamethylheptasiloxane</td>
<td>(CH₃)₇SiO₇</td>
<td>79 ± 2</td>
<td>92.6 (20 mm)</td>
<td>1.0143</td>
<td>1.3960</td>
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<tr>
<td>Decamethylheptasiloxane</td>
<td>(CH₃)₇SiO₇</td>
<td>–80</td>
<td>106.5 (10 mm)</td>
<td>0.8993</td>
<td>1.3895</td>
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<td>Decamethyloxasiloxane</td>
<td>(CH₃)₈SiO₈</td>
<td>–80</td>
<td>245</td>
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<td>–</td>
<td>–</td>
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<tr>
<td>Dodecamethyloxasiloxane</td>
<td>(CH₃)₈SiO₈</td>
<td>25</td>
<td>128 (20 mm)</td>
<td>0.9762</td>
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<td>Tetradecamethylcycloheptasiloxane</td>
<td>(CH₃)₉SiO₉</td>
<td>30–32</td>
<td>154 (20 mm)</td>
<td>0.9730</td>
<td>1.4040</td>
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<td>Hexadecamethylcyclononasiloxane</td>
<td>(CH₃)₁₀SiO₁₀</td>
<td>31.5</td>
<td>175 (20 mm)</td>
<td>–</td>
<td>–</td>
<td>22.24</td>
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<tr>
<td>Octadecamethylcyclomonasiloxane</td>
<td>(CH₃)₁₀SiO₁₀</td>
<td>31.5</td>
<td>163 (20 mm)</td>
<td>–</td>
<td>–</td>
<td>22.24</td>
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### Table 82

**Physical Properties of Organosiloxanes Containing Chlorine and Various Functional Groups and Radicals**

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<th>Name</th>
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<td>Chloromethylpentamethyldisiloxane</td>
<td>CICH(CH₃)₂SiOS(CH₃)₂</td>
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<tr>
<td>Di-(chloromethyl)-tetramethyldisiloxane</td>
<td>CICH(CH₃)₂SiOSi(CH₃)₂CH₂Cl</td>
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<tr>
<td>1,2-Di-(dichloromethyl)-tetramethyldisiloxane</td>
<td>Cl₂CH(CH₃)₂SiOSi(CH₃)₂CH₂Cl</td>
</tr>
<tr>
<td>1,3-Di-(chloromethyl)-hexamethytrisiloxane</td>
<td>CICH(CH₃)₂SiOSi(CH₃)₂Si(CH₃)₂CH₂Cl</td>
</tr>
<tr>
<td>1,4-Di-(chloromethyl)-octamethyltetrasiloxane</td>
<td>CICH(CH₃)₂SiO(Si(CH₃)₂CH₂Cl)</td>
</tr>
<tr>
<td>1,5-Di-(chloromethyl)-decamethylpentasiloxane</td>
<td>CICH(CH₃)₂SiOSi(CH₃)₂Si(CH₃)₂CH₂Cl</td>
</tr>
<tr>
<td>1,6-Di-(chloromethyl)-dodecamethylhexasiloxane</td>
<td>CICH(CH₃)₂SiOSi(CH₃)₂Si(CH₃)₂CH₂Cl</td>
</tr>
<tr>
<td>Heptamethyl-2-chloromethytrisiloxane</td>
<td>(CH₃)₂SiOSiOSi(CH₃)₂</td>
</tr>
<tr>
<td>Octamethyl-2,3-di-(chloromethyl)-tetrasiloxane</td>
<td>(CH₃)₂SiO(Si(CH₃)₂CH₂Cl)Si(CH₃)₂CH₂Cl</td>
</tr>
<tr>
<td>Nonamethyl-2,3,4-tri-(chloromethyl)-pentasiloxane</td>
<td>(CH₃)₂SiO(Si(CH₃)₂CH₂Cl)Si(CH₃)₂CH₂Cl</td>
</tr>
<tr>
<td>Decamethyl-2,3,4,5-tetra-(chloromethyl)-hexasiloxane</td>
<td>CICH(CH₃)₂SiO(Si(CH₃)₂CH₂Cl)Si(CH₃)₂CH₂Cl</td>
</tr>
<tr>
<td>1,2,3-Tri-(chloromethyl)-pentamethyltrisiloxane</td>
<td>CICH(CH₃)₂SiO(Si(CH₃)₂CH₂Cl)Si(CH₃)₂CH₂Cl</td>
</tr>
<tr>
<td>1,2,3,4-Tetra-(chloromethyl)-hexamethytrisiloxane</td>
<td>CICH(CH₃)₂SiO(Si(CH₃)₂CH₂Cl)Si(CH₃)₂CH₂Cl</td>
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<td>1,2,3,4,5-Penta-(chloromethyl)-heptamethylpentasiloxane</td>
<td>CICH(CH₃)₂SiO(Si(CH₃)₂CH₂Cl)Si(CH₃)₂CH₂Cl</td>
</tr>
<tr>
<td>1,2-Di-(α-chloromethyl)-tetramethoxydisiloxane</td>
<td>CICH₂CH₃Si(OSi(CH₃)₂CH₂Cl)</td>
</tr>
<tr>
<td>1,2-Di-(α-chloroethyl)-tetraethoxydisiloxane</td>
<td>CICH₂CH₃Si(OSi(CH₃)₂CH₂Cl)</td>
</tr>
<tr>
<td>1,2-Di-(β-chloromethyl)-tetraethoxydisiloxane</td>
<td>CICH₂CH₃Si(OSi(CH₃)₂CH₂Cl)</td>
</tr>
<tr>
<td>1,2-Di-(β-chloroethyl)-tetraethoxydisiloxane</td>
<td>CICH₂CH₃Si(OSi(CH₃)₂CH₂Cl)</td>
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<td>Di-(pentachloro)tetra(2-hydroxydiethyl)disiloxane</td>
<td>[HOCH₂CH₃]₂SiOSi(OSi(CH₃)₂CH₂Cl)</td>
</tr>
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<td>1,2-Dihydroxymethyltetramethyldisiloxane</td>
<td>[HOCH₂CH₃]₂SiOSi(OSi(CH₃)₂CH₂Cl)</td>
</tr>
<tr>
<td>1,2-Dihydroxytetraphenyltrisiloxane</td>
<td>[HOCH₂CH₃]₂SiOSi(OSi(CH₃)₂CH₂Cl)</td>
</tr>
<tr>
<td>Carboxymethylpentamethyldisiloxane</td>
<td>[HOCH₂CH₃]₂SiOSi(OSi(CH₃)₂CH₂Cl)</td>
</tr>
<tr>
<td>Acetoxyethylpentamethyldisiloxane</td>
<td>[HOCH₂CH₃]₂SiOSi(OSi(CH₃)₂CH₂Cl)</td>
</tr>
<tr>
<td>1,2-Diacetoxyethyltetramethyldisiloxane</td>
<td>[HOCH₂CH₃]₂SiOSi(OSi(CH₃)₂CH₂Cl)</td>
</tr>
<tr>
<td>1,2-Dimethylethoxytrisiloxane</td>
<td>[HOCH₂CH₃]₂SiOSi(OSi(CH₃)₂CH₂Cl)</td>
</tr>
<tr>
<td>1,3-Dimethylhexamethoxytrisiloxane</td>
<td>[HOCH₂CH₃]₂SiOSi(OSi(CH₃)₂CH₂Cl)</td>
</tr>
<tr>
<td>1,2-Dimethyltetraoxytrisiloxane</td>
<td>[HOCH₂CH₃]₂SiOSi(OSi(CH₃)₂CH₂Cl)</td>
</tr>
<tr>
<td>1,2-Dimethyltetraoxydibutylsiloxane</td>
<td>[HOCH₂CH₃]₂SiOSi(OSi(CH₃)₂CH₂Cl)</td>
</tr>
<tr>
<td>1,2-Dimethyltetramethoxydibutylsiloxane</td>
<td>[HOCH₂CH₃]₂SiOSi(OSi(CH₃)₂CH₂Cl)</td>
</tr>
<tr>
<td>1,2-Dihydroxymethylphenyltrisiloxane</td>
<td>[HOCH₂CH₃]₂SiOSi(OSi(CH₃)₂CH₂Cl)</td>
</tr>
<tr>
<td>1,2-Dihydroxydiethylphenyltrisiloxane</td>
<td>[HOCH₂CH₃]₂SiOSi(OSi(CH₃)₂CH₂Cl)</td>
</tr>
<tr>
<td>1,2-Di-(nitrophenyl)carboxymethyl-1,2-tetramethyldisiloxane</td>
<td>[HOCH₂CH₃]₂SiOSi(OSi(CH₃)₂CH₂Cl)</td>
</tr>
<tr>
<td>1,3-Dihydroxyhexaphenytrisiloxane</td>
<td>[HOCH₂CH₃]₂SiOSi(OSi(CH₃)₂CH₂Cl)</td>
</tr>
<tr>
<td>1,3-Dihydroxyhexabenzytrisiloxane</td>
<td>[HOCH₂CH₃]₂SiOSi(OSi(CH₃)₂CH₂Cl)</td>
</tr>
<tr>
<td>Freezing Point °C</td>
<td>Boiling Point °C</td>
</tr>
<tr>
<td>------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>151.6–151.8</td>
<td>204.5</td>
</tr>
<tr>
<td>90</td>
<td>110 (40 mm)</td>
</tr>
<tr>
<td>79</td>
<td>150 (40 mm)</td>
</tr>
<tr>
<td>94</td>
<td>142 (40 mm)</td>
</tr>
<tr>
<td>35</td>
<td>168 (40 mm)</td>
</tr>
<tr>
<td>77</td>
<td>190 (40 mm)</td>
</tr>
<tr>
<td>223 (40 mm)</td>
<td>0.996</td>
</tr>
<tr>
<td>85</td>
<td>102 (40 mm)</td>
</tr>
<tr>
<td>77</td>
<td>162 (40 mm)</td>
</tr>
<tr>
<td>85</td>
<td>210 (40 mm)</td>
</tr>
<tr>
<td>77</td>
<td>251 (40 mm)</td>
</tr>
<tr>
<td>176 (40 mm)</td>
<td>1.122</td>
</tr>
<tr>
<td>167 (5 mm)</td>
<td>1.157</td>
</tr>
<tr>
<td>210 (5 mm)</td>
<td>1.182</td>
</tr>
<tr>
<td>108 (2 mm)</td>
<td>1.176</td>
</tr>
<tr>
<td>132–133 (5 mm)</td>
<td>1.089</td>
</tr>
<tr>
<td>133 (3 mm)</td>
<td>1.189</td>
</tr>
<tr>
<td>134–135 (1 mm)</td>
<td>1.091</td>
</tr>
<tr>
<td>180–181 (7 mm)</td>
<td>1.045</td>
</tr>
<tr>
<td>178–183 (1 mm)</td>
<td>—</td>
</tr>
<tr>
<td>5</td>
<td>0.975</td>
</tr>
<tr>
<td>113</td>
<td>—</td>
</tr>
<tr>
<td>17</td>
<td>—</td>
</tr>
<tr>
<td>180 (785 mm)</td>
<td>0.902</td>
</tr>
<tr>
<td>250</td>
<td>0.993</td>
</tr>
<tr>
<td>62 (1 mm)</td>
<td>1.0179</td>
</tr>
<tr>
<td>82 (2 mm)</td>
<td>1.0488</td>
</tr>
<tr>
<td>100 (20 mm)</td>
<td>1.3886</td>
</tr>
<tr>
<td>160 (4 mm)</td>
<td>1.9104</td>
</tr>
<tr>
<td>175–177 (2 mm)</td>
<td>0.9066</td>
</tr>
</tbody>
</table>

Table 82 (cont'd)
diethylsiloxane is formed from dibenzylethylchlorosilane (Bibl.16). On the hydroly-
ysis of benzylethylbutylchlorosilane, dibenzyldiethyl dibutylsiloxane is formed.
The presence of an unsaturated organic radical in the chloride molecule does not
change the course of the hydrolysis reaction. On hydrolysis of allyldimethylchloro-
silane in an acid medium, diallyltetramethylsiloxane is formed in good yield. The
formation of polymeric products on account of a reaction at the place of the double
bond has not been observed (Bibl.18).

The only hexaalkyldisiloxane with a triple bond in the organic radical that is
known today is hexaethynyldisiloxane, synthesized by Vol'nov and Reutt (Bibl.19),
by hydrolysis of the reaction mass obtained after the reaction between $\text{SiCl}_4$ and
acetylene magnesium bromide, by the following technique.

Preparation of hexaethynyldisiloxane. To 1 mol of $\text{CH} = \text{CHMgBr}$, dissolved in ether,
0.175 mol of $\text{SiCl}_4$ is gradually added. After the addition has been completed, the
mixture is heated 3 hours on the water bath, and is then decomposed by water. The
ether layer is separated and the solvent distilled off. The residue, consisting of
hexaethynyldisiloxane, is recrystallized from ethanol.

Hexaethynyldisiloxane forms yellowish-white crystals of melting point 19–20°C,
which are readily soluble in ether, benzene, toluene, petroleum ether, and chloro-
form.

Table 81 gives the physical properties of certain low-molecular organosiloxanes.

The organosiloxanes with a chlorine atom in the radical are of particular in-
terest, for chlorine has a substantial influence on the physical and other proper-
ties of these compounds, increasing the force of intermolecular interaction (cohe-
sive forces). Chloromethylmethylsiloxanes of three types may be prepared:

\[
\begin{align*}
\text{ClCH}_2\text{Si(CH}_3\text{)}_2\text{O} & \text{Si(CH}_3\text{)}_2\text{CH}_2\text{Cl} \\
(\text{CH}_3\text{)}_2\text{SiO} & \text{Si(CH}_3\text{)}_2\text{CH}_2\text{Cl} \\
\text{ClCH}_2(\text{CH}_3\text{)}_2\text{SiO} & \text{Si(CH}_3\text{)}_2\text{CH}_2\text{Cl}
\end{align*}
\]
Polymers of the first type have been prepared by 2 hour boiling of a mixture of 178 g (1.24 mols) of dimethylchloromethylchlorosilane and 46 g (0.62 mol) of hexamethylcyclotrisiloxane in aqueous-alcoholic solution. The reaction mixture was then washed with water, dried over calcium chloride, and fractionated.

Polymers of the second type have been prepared by 3.5 hour boiling of an aqueous-alcoholic solution of a mixture of 162 g (1 mol) of hexamethyldisiloxane and 163.5 g (1 mol) of chloromethylmethyldichlorosilane. The reaction mixture was then washed with water, dried over calcium chloride, and fractionated.

Polymers of the third type have been prepared by reacting a mixture of 2 mols of dimethylchloromethylchlorosilane and 1 mol of chloromethylmethyldichlorosilane, followed by addition to aqueous alcohol. The mixture so obtained was then stirred. Its further treatment was similar to the preceding.

It is interesting to note that the degree of polydisperseness of the reaction products is the same in all three cases, and it was only in the preparation of polymers of the first type that traces of cyclic products were found in the reaction mixture. This phenomenon is to a certain extent in contradiction to the literature statements that cyclic polymers are formed in cases where the system is in the equilibrium state. It is possible that the formation of polymers in this case may be hindered by the large size of the CH₂Cl group.

The polymers of the first group have specific refractive indices and activation energies of viscous flow that are very close together.

The chlorine content of the polymers was determined by heating a weighed sample portion of the polymer with a known quantity of a solution of KOH in diethylene glycol in a closed flask at 150-175°C, and titration of the excess alkali against a titrated solution of acid. The polymers of the third group form gels when this determination is made.

Titration of alkali against acid is difficult in the presence of a gel and gives fluctuating results. The molecular weight of polymers of the third type was
ebulliometrically determined. The values of the molecular weights were found by extrapolation of the experimental data to zero concentration.

Table 82 gives the physical properties of organosiloxanes containing chlorine together with various functional groups in the radicals.

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   68, 156, 975, 1380 (1946); 70, 443 (1948)


21. Pape - Ber., 14, 1874 (1881); Ann., 222, 355 (1884)
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CHAPTER X

HIGH-MOLECULAR COMPOUNDS CONTAINING SILICON

Silicon forms high-polymer compounds of two types, inorganic and organic. This Chapter is devoted mainly to the chemistry of the high-molecular organosilicon compounds.

Organosilicon polymers are complex compounds, whose molecular chains are constructed of alternating silicon and oxygen atoms, or of silicon and carbon, silicon and nitrogen, silicon and sulfur, etc., side organic radicals or groups being present at the same time.

Organosilicon high-polymer compounds constitute a new branch of the chemistry of polymers, which possess properties of exceptional practical importance; they are heat-resistant, moisture-resistant, have low dielectric losses and high electrical resistivities, high electrical breakdown strength, exceptional anti-sparking and anti-arcing properties, considerable compressability under high pressures, good resistance to freezing, etc.

A large variety of high-polymer products are already being produced today on an industrial scale: rubbers of exceptional thermal stability and resistance to freezing; resins for the production of heat-resistant lacquers and plastics, and electrical insulation; liquids with a low temperature-dependence of viscosity, for water-repellent treatment of materials; lubricating oils with low freezing points and high thermal stability.

Organosilicon polymeric compounds broaden the range of working temperatures to from -100°C to +300°C, which lie far beyond the limits within which organic polymers can be used. These properties are due primarily to the chemical composition and the structure of the molecular chains, in which the silicon atom is most often bound to oxygen atoms. This structure was previously known only in high-polymer
inorganic products, such as glass, quartz, etc.

The high-polymer organosilicon compounds whose molecular chain consists of alternating atoms - Si - O - Si - O - Si -, known today under name of polyorganosiloxanes, are widely available. These polymers are of very great technological importance, and therefore will be given particular attention in this Chapter.

Before beginning our discussion of polymeric organosilicon compounds, it appears to us to be advisable to discuss the oxygen-containing inorganic polymeric silicon compounds of the type \((\text{SiO}_2)_n\) and water-glass, and also to acquaint ourselves, from the example of carborundum, with the properties of polymers containing the Si - C bond. Acquaintance with these substances will enable us to compare their properties with those of the polymeric organosilicon compounds, and to understand certain specific peculiarities of the formation and chemical properties of the polyorganosiloxanes, which is the branch of greatest practical importance and theoretical interest in the chemistry of the organosilicon polymers.

Organosilicon polymers may be divided into the following groups, according to their chain structure: polymeric compounds whose chains contain silicon - oxygen - silicon; polymeric compounds with chains containing silicon - carbon - silicon - oxygen; polyorganometallosiloxanes with chains containing silicon - oxygen - metal - oxygen - silicon, Si - O - Me - O - Si.

**Polymeric Compounds with Silicon - Oxygen - Silicon Chains**

Organosilicon polymeric compounds with molecular chains constructed of silicon and oxygen atoms may be classified as follows:

1. Derivatives of orthosilicic acid esters:

\[
\begin{align*}
&\text{OR} \quad \text{OR} \quad \text{OR} \\
&\quad \quad \text{1} \quad \text{2} \quad \text{3} \\
&\text{OR} \quad \text{OR} \quad \text{OR}
\end{align*}
\]

linear polymers

F-TS-9191/V 701
2. Derivatives of monoalkyl- or monoaryl-substituted esters of orthosilicic acid or of monoalkyl- or monoaryl-halosilanes:

3. Derivatives of dialkyl-(diaryl)-substituted esters of orthosilicic acid or of dialkyl-(diaryl)-halosilanes:

The cocondensation of alkyl-(aryl)-silanetriols with dialkyl-(diaryl)-silanediols leads to the formation of compounds with molecules consisting of siloxane chains of cross-linked structure:
Polymeric Compounds with Silicon – Carbon – Silicon – Oxygen Chains

By the introduction of organic groups into molecules with siloxane bonds, a new class of high-molecular organosilicon compounds with a mixed siloxancarbon chain may be prepared:

\[
\cdots \text{Si} - \text{R} - \text{Si} - \cdots
\]

**Polycrorganometallosiloxanes**

Polymeric compounds with silicon – oxygen – metal – oxygen chains are obtained by hydrolysis of alkyl-(aryl)-halosilanes with metallic salts.

Polycrorganometallosiloxanes have the following structure:

\[
\cdots \text{Si} - \text{R} - \text{Si} - \cdots
\]

where \( \text{R} \) = Al, Ti, etc.

**Polymeric Inorganic Compounds of Silicon**

In the macromolecule of silica \((\text{SiO}_2)_n\) and of the silicates, each silicon atom is bound to four oxygen atoms, while each oxygen atom is bound to two silicon atoms. Thus, in \((\text{SiO}_2)_n\), all the bonds between adjacent atoms are completely saturated by
the valences of silicon and oxygen (Fig.1.1).

The lattices of solid SiO₂ and solid CO₂ differ sharply from each other. The CO₂ lattice is molecular.

SiO₂ (silica) does not constitute a single molecule, but a high-polymer compound with a high melting point \((1625°C)\).

The energy of the single bond C - O is 75 kcal, while the energy of the Si - O bond amounts to 89 kcal. This difference in bond energies is due to the character of the Si - O bond being considerably closer to an ionic bond than the C - O bond, owing to the fact that silicon is more highly electropositive (the energy of ionization of silicon being 71.4 kcal less than that of carbon).

**Lower Oxygen Compounds of Silicon**

The lowest representative of the silicon oxides is SiO. In vapor form, SiO is an individual compound, as has been established by X-ray analysis. Its spectrum has absorption bands at 2141, 2342, 2299, 2256, 2215 Å. \((\text{SiO}_2)_n\) remains solid up to the melting point, but when heated above 1700°C, it begins to sublime vigorously (Fig.1.2).

**Quartz**

Silicon dioxide is trimorphous; it is encountered in the form of the minerals: quartz, tridymite and cristobalite. These minerals also form a few other intermediate forms. In tridymite and cristobalite the optical properties change in jumps, in the former, at 117°C and 163°C; in the latter, at 190°C and 280°C; the volume of quartz changes so greatly at around 575°C that on further heating (above this temperature) its crystals partially crumble away. At ordinary temperatures quartz is a stable form. If silica gel is heated with water containing carbon dioxide to 275°C, only quartz crystals are obtained. At 875°C quartz passes over into tridymite, but the reverse transformation of tridymite into quartz, in the absence of a solvent, has not yet been observed. Solvents encouraging the transformation of tridymite into
quartz are molten alkali-metal chlorides, borax, and especially tungstates or vanades of the alkali metals.

The transition temperatures of the various modifications of quartz are as follows:

\[
\begin{align*}
\beta\text{-quartz} & \quad 573^\circ\text{C} \quad \gamma\text{-quartz} & \quad 870^\circ\text{C} \quad \alpha\text{-tridymite} & \quad 1470^\circ\text{C} \quad \gamma\text{-christobalite} & \quad 1710^\circ\text{C} \quad \text{melts}
\end{align*}
\]

The transformations of \(\alpha\)- and \(\beta\)-quartz into each other are accomplished without disturbance of the external form of the crystals. Since the individual particles still preserve their mutual positions, the transition in one direction or the other, at temperatures above or below 575°C, takes place easily.

The modifications with the lowest vapor pressure at a given temperature are stable. It must be noted that the transition of low-temperature modifications into high-temperature modifications, or in the opposite direction, is accomplished with great ease and rapidity within one and the same variety of silica, for instance the transition from \(\alpha\)-quartz into \(\beta\)-quartz. This is because such a transition involves only a shift and rotation of the silicon-oxygen tetrahedra in the crystal. For the transition of one variety of silica into another, for instance from \(\alpha\)-quartz into \(\alpha\)-tridymite, the bonds between the separate silicon-oxygen tetrahedra must be broken, and new bonds must be formed. This makes such transitions extremely slow, as is proved by the fact that all varieties of silica exist in the form of minerals for hundreds of thousands of years.

The structure of the low-temperature modifications of crystalline silica has not yet been definitively elucidated.

Tridymite and christobalite have a hexagonal and cubic structure respectively, and therefore their densities are close together. Quarts, however, has a considerably more compact structure, and accordingly has a higher density and a higher refractive index.
Table 83 gives the physical properties of the different modifications of silicon dioxide.

### Table 83

Physical Properties of the Different Modifications of Silicon Dioxide

<table>
<thead>
<tr>
<th>Modification</th>
<th>Density</th>
<th>Refractive Index</th>
<th>Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$N_r$</td>
<td>$N_p$</td>
</tr>
<tr>
<td>α-Quartz</td>
<td>2.600</td>
<td>1.5400</td>
<td>1.53</td>
</tr>
<tr>
<td>α-Tridymite</td>
<td>2.28</td>
<td>1.4775</td>
<td>—</td>
</tr>
<tr>
<td>α-Christobalite</td>
<td>2.210</td>
<td>1.466</td>
<td>—</td>
</tr>
<tr>
<td>β-Quartz</td>
<td>2.650</td>
<td>1.553</td>
<td>1.544</td>
</tr>
<tr>
<td>β₁-Christobalite</td>
<td>2.30</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Quartz glass</td>
<td>2.320</td>
<td>1.487</td>
<td>1.484</td>
</tr>
</tbody>
</table>

Amorphous fused glass (quartz glass) was formerly considered a supercooled liquid or a microcrystalline substance. Against this view, evidently, are the high softening point and the great hardness of fused quartz.

The melting point of α-christobalite is 1713°C; at this temperature it undergoes transition into a viscous quartz glass.

Silicon dioxide has no definite melting point, because it contains several modifications at the same time, in an inconstant quantitative ratio; on heating, the substance gradually softens, like glass; at 1500°C it already becomes plastic, and when heated still further it may be drawn out into thin filaments. Around 1780°C it becomes completely liquid. Even before the time of fusion has arrived, therefore, vessels of silicon dioxide may be fashioned; by this method of manufacture they are not transparent, like "quartz glass", which is first brought into a state of complete fusion, but has the appearance of an opaque quartz porcelain with a silky luster. If silicon dioxide is vaporized at a temperature over 1750°C (the boiling point under atmospheric pressure is 2230°C), then the vapor only partially condenses in the form of tridymite, while the remainder forms a glassy mass. This glassy mass is distinguished by its very small changes with temperature fluctuations; its coefficient of expansion is only 1/18 that of glass, so that heated quartz vessels may be cooled by rapidly plunging them into water without danger of cracking them. Accord-
ing to present ideas, amorphous quartz glass is a system of silicon-oxygen tetra-
hedra bound to each other through common oxygen atoms and having a disordered ar-
rangement (Bibl.4). These ideas are based primarily on the study of X-ray pictures
of these glasses.

Properties of Quartz

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus of elasticity at 0°C, kg/mm²</td>
<td>10300</td>
</tr>
<tr>
<td>Tensile strength, kg/mm²</td>
<td>16.3 (12.6)</td>
</tr>
<tr>
<td>Coefficient of expansion at 0°C</td>
<td>0.00000748</td>
</tr>
<tr>
<td>Specific heat, cal/°C</td>
<td>0.18</td>
</tr>
</tbody>
</table>

Silicic anhydride ($\text{SiO}_2$) in the form of crystals may be prepared artificially
from silica gel in an alkaline medium. Such a crystal is formed on the cover of a
bomb to which a thin quartz plate has been attached. Such a plate gradually becomes
thicker owing to the deposition on it of silica from the solution.

Silicon dioxide, especially in crystalline form, is little subject to the ac-
tion of chemical reagents (except alkalies). The action of alkalies on silica may be
explained by the fact that it is the anhydride of silicic acid. The chemical activ-
ity of silica toward various reagents depends on the form of the silica (Bibl.5),
and increases in the following order:

quartz < tridymite < christobalite < fused quartz < hydrated silica

Quartz dissolves very slowly in water; the temperature of the water affects
the rate of dissolution, as does, to a lesser degree, the pressure.

Silica gel dissolves relatively fast in water, and its solubility does not de-
pend on the method of preparation of the gel. Only the time required for the solu-
tion to reach full saturation depends on that method. Apparently the relative sur-
face area of the gel particles is of primary importance.

Of the acids, only HF acts on quartz. The rate of dissolution of silica in hy-
drofluoric acid depends on the activity of the particular form of silica involved.
Silica gel forms colloidal solutions in weak hydrochloric and sulfuric acids.

Fluorine is the only halogen that acts on SiO₂ under ordinary conditions. When mixed with carbon, at a red heat, silica also reacts with chlorine (Bibl.7) and bromine (Bibl.8).

Sulfur, H₂S, or CS₂, acting on silica at 800-1100°C, forms long silky crystals of silicon disulfide (Bibl.9). At high temperature, nitrogen also acts on silica, forming silicon nitride (Bibl.10).

Certain halogen compounds also act on silica. When silica is heated with ammonium fluoride, SiF is formed (Bibl.11). SiCl₄ is formed when PCl₃ or PCl₅ act on silica (Bibl.12). SiF₄ is formed from silica under the action of PF₃ or CF₄. According to Demarie (Bibl.13), CCl₄ also acts on silica at a red heat, slowly forming SiCl₄. There are statements, however, that CCl₄ acts only on SiO₂ that is chemically combined with Al₂O₃, and therefore treatment with CCl₄ at a red heat has been proposed as a method of removing the free and bound SiO₂ from bauxites.

The rate of dissolution of silica in alkalies depends on its activity; quartz is dissolved very slowly, silica gel very fast. Finely powdered quartz is also dissolved relatively fast. Silica dissolves very slowly in hydrated oxides of alkaline-earth metals (Bibl.15). Ca(OH)₂ in aqueous solution acts on silica, a fact which is used in practice in the manufacture of sand-lime brick. Calcium silicates are formed by such action.

Silica gel reacts appreciably with calcium oxide at 1600°C, while fused quartz reacts very little; christobalite forms a silicate at 1400°C. Silica gel reacts with barium oxide already at 900°C; but with magnesium oxide no signs of reaction can be detected at that temperature. The action of the alkali-metal carbonates, on fusion, is similar to that of the alkalies themselves (Bibl.16). Sodium sulfate begins to react with silica at a temperature between 1120 and 1130°C.

In reactions taking place in aqueous solutions, the principal role is played by the fact that silicic acid has exceptionally weak acidic properties and is dis-
placed from its salts even by carbonic acid. On fusion, the most essential property of silicic acid is its nonvolatility at high temperatures, which results in its displacing even strong acids, like sulfuric, from their salts.

Silicon Hydroxides

The hydrates of silicon dioxide are obtained, not by direct addition of water to the dioxide but by a different method. In contrast to $H_2CO_3$, they are more stable; and the fact that they are always obtained in the colloidal state is particularly characteristic. They are weak acids, weaker even than carbonic acid, since in one and the same group of the periodic system, the elements of negative character always weaker with increasing atomic weight. The alkali salts of silicic acid are strongly dissociated. This is confirmed by the fact that the heat of neutralization of a dilute solution of the acid by NaOH is almost zero, and the electrical conductivity of the solution is almost the same as that of the caustic soda it contains; in 1/8N solution, hydrolysis of the sodium salt may be considered to be practically complete; while hydrolysis of salts of weaker bases is detected only at higher concentrations. A solution of sodium silicate thus contains at the same time free caustic soda, colloidal silicic acid, and unhydrolyzed sodium silicate. The caustic soda can be removed by dialysis from such solutions, while the silicic acid does not pass the membrane.

By dialysis of a solution of sodium silicate a very pure colloidal solution of silicic acid can be prepared.

The hydroxides of silicon may also be prepared by the action of acids on sodium silicate:

$$ Si(ONA)_4 + 4HCl \rightarrow Si(OH)_4 + 4NaCl $$

In this case the hydroxides are often obtained, not in the form of a solution, but in the form of a gel; depending on the concentration, the solution either re-
mains transparent or gels. For instance, if a 10% solution is poured, with shaking, into HCl of the same concentration, a completely transparent sol may be prepared, which can then be separated by dialysis from the NaCl.

A solution of silicic acid at first contains acid of low molecular weight, which polymerizes only after a certain time. This is due to the gradual rise in the freezing point of the solution after the HCl is added to the water glass to be dissolved, and also due to the passage of rather considerable quantities of silicic acid through the membrane on immediate dialysis (Bibl.17).

According to some determinations, the molecular weight of silicic acid in its sols is as much as 50,000. The rate of polymerization of silicic acid depends on the hydrogen ion concentration. If SiCl$_4$ is hydrolyzed, the HCl formed rapidly induces polymerization. But if silver oxide is added when SiCl$_4$ vapor is passed into the water to hold the pH constant in the range 2 - 2.5, then a liquid is obtained which, according to cryoscopic determination, contains as much as 80% of monomolecular silicic acid and a solution of the dimer of silicic acid. In this case the HCl must be completely eliminated. (Bibl.18).

The dimer of silicic acid, to which the formula 0[Si(OH)$_3$]$_2$ has been attributed, passes completely through the dialysis membrane; polymers of silicic acid with a higher molecular weight also pass the membrane, but more slowly. Protein is precipitated by polymeric silicic acid containing not more than six silicon atoms in the molecule.

The existence of two different hydrates of silicic acid is known (Bibl.17): the hydrate of metasilicic acid H$_2$SiO$_3$(probably polymerized and therefore insoluble), and the hydrate of disilicic acid, H$_2$Si$_2$O$_5$. These two hydrates, prepared by decomposing their synthetic sodium salts by conc. sulfuric acid, differ not only in the course of the dehydration curve, but also in the fact that the meta-acid, according to the X-ray picture, is amorphous, while the di-acid has a crystalline structure. The gels of silicic acid formed from silicon tetrahalides by hydrolysis at O°C,
contain the hydrate \( (\text{SiO}_2 \cdot \text{H}_2 \text{O})_x \) (Bibl.19). If the reaction of formation of silicic acid is conducted in an anhydrous medium (Bibl.20), then a precipitate containing only slightly more water than \( (\text{Si}_x \cdot \text{H}_2 \text{O})_2 \) is obtained instead of \( \text{Si} \cdot (\text{CH})_4 \), which should have been formed according to the equation:

\[
\text{SiCl}_4 + 4(\text{C}_4\text{H}_8)\text{COH} \rightarrow \text{Si(OH)}_4 + 4(\text{C}_4\text{H}_8)\text{CCI}
\]

Gels prepared by precipitation always contain electrolytes that were present in the solution. They can be removed with more or less trouble. For instance, it is rather easy to remove the sodium chloride from the gel prepared by the action of HCl on sodium silicate, by dialysis, but it is extremely difficult to free the gel from the sodium ion, which indicates the presence of a sodium compound. Sols not containing alkalies may be prepared by boiling an ester of orthosilicic acid with water:

\[
\text{Si} \cdot (\text{OC}_4\text{H}_8)_4 + 4\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 + 4\text{C}_4\text{H}_8\text{OH}
\]

On evaporation, the sols also form a gel. But the concentration of these sols is lower than the concentration that can be attained by the action of electrolytes. It may be brought up to 14%, and the immediate formation of a gel does not occur. The ease of gelation increases with the concentration of the solution, and also with the temperature at which the experiment is conducted.

The action of acids, salts and alkalies does not cause instantaneous coagulation of a sol of silicic acid, and sometimes gels are even made more stable by such treatment; in other cases their precipitation sets in after a certain time has elapsed, and is accelerated with decreasing content of these substances.

In a study of the structure of the gel of silicic acid, Van Bommelen showed that its properties do not depend on the water content alone. The vapor pressure of
gels at various water contents was determined; for this purpose the gels were kept over sulfuric acid of known concentration (having a definite water vapor pressure), and then, when the loss of weight of the gel had become very small after its prolonged stay over this sulfuric acid, the water-vapor pressure of the gel was taken as equal to the water-vapor pressure of the sulfuric acid. Various gels of the silicic acids were dehydrated; then these gels were rehydrated by keeping them over sulfuric acid of higher water content. It was found that dehydration and hydration are not always reversible. The gels of the silicic acids may be very rich in water, in contrast, for instance, to the gels of certain hydrates of metals. Under certain conditions, a silicic acid gel may contain, to each mol of SiO₂, up to 330 mols of water, which may in part be removed by mechanical squeezing. With a content of 30 mols of water per mol of SiO₂ a gel may be cut, with a content of 10 mols of water per mol of SiO₂, it becomes brittle, while with a content of 6 mols of water per mol of SiO₂, it can be ground into a dry powder.

In Figure 34, the corresponding water vapor pressure is plotted on the ordinate axis, and the water content of the gel on the abscissa axis. If the dehydration of a silicic acid gel containing much water begins at the point A₀, the vapor pressure will fall sharply (with the loss of water) until the point O is reached. At this point, as it were, a change-over takes place; the existence of this point was formerly taken as a proof of the existence of definite hydrates. But the position of this point may vary markedly, according to the experimental conditions, and it can be shifted at will more or less to the left. At the point O the silicic acid gel begins to show turbidity. The turbidity increases at first, and then de-
creases, disappearing entirely at the point $O_1$. Van Bommelen calls the points $0$ and $O_1$ "turning points". When the second turning point $O_1$ has been passed, on further lowering of the vapor pressure, the water loss again considerably decreases, the curve is inflected upward, and terminates at the point $A$, corresponding to a product containing a very small amount of water.

Then hydration begins (curve $Z$). From $A_3$ to $O_1$ the process of hydration completely corresponds to the preceding process of dehydration. The two curves $O_1A_3$ and $A_3O_1$ coincide. Here the processes of liberation and addition of water are reversible. But at the point $O$ this reversibility ceases: an increase in the water-vapor pressure results in the formation of products (points on the $Z$ curve) with a lower water content than those that were formed during dehydration (the point $A_2$) at the same vapor pressure. On further increase in the water-vapor pressure, the water content rises somewhat, but a higher pressure is always required for rehydration than was required to obtain the dehydration product of the same composition.

The point $O_2$ at which the turbidity disappears, observed on the $Z_2$ curve, lies far above the point $O$ at which this phenomenon was observed on the first path. If hydration is continued beyond this point, water is still absorbed, but not enough to form a product containing 300 mols of water per mol of $SiO_2$ (curve $Z_3$).

Similarly, if dehydration stops at the point $O$, and then rehydration is performed, it will proceed, not back along the path $A_1$, but along the path $Z_4$ instead. Even if the point $C$ has not been reached in the dehydration, and it is stopped at the point $A_1$, a renewal of hydration leads not to $A_0$, but to $Z$. Consequently $O_1A_3$ is the only part of the curve that is reversible.

In general the curve of dehydration is not the same in all silicic acid gels, nor do the turning points lie at one and the same position. Their position probably depends on many factors, for instance on the method of preparing the gels, on their age, on the rate of dehydration and on the temperature at which it proceeds. The point $O$ is reached the earlier (lies the more to the left) the lower the concentra-
tion of the solution from which the gel was precipitated, the more rapidly the de-
hydration was conducted, the shorter the time elapsed since the preparation of the
gel, and the lower the temperature during dehydration. If the point 0 is very close
to $G_1$, the $A$ curve almost coincides with the $Z$ curve.

A silicic acid gel that has long been calcined at a high temperature will not
in general again absorb water. It follows that the turning points are not points of
phase-transition, and it may be supposed that most of the water is not bound chemi-
cally, but is held by adsorption, which is the firmer, the less water there is.

To explain the existence of turning points, indicating a change in the charac-
ter of the adsorption under certain conditions, the structure of gels must be con-
sidered in detail.

A silicic acid gel prepared from a very dilute solution, when viewed under the
ultramicroscope, is at first floccular, but afterward becomes granular. But if the
gel is dried, turbidity begins to appear at a 40% water content. It has been stated
above that, on further drying, this turbidity again disappears. If a transparent gel,
obtained in this way, is impregnated with benzene, then its structure at this time
will recall a honeycomb. It is interesting to note that the structure of a gel re-
calling a honeycomb begins to be visible only at this middle stage of filling with
liquid, but not when the gel is either dried out, or is in a strongly swollen state.
This fact was long explained by the difference between the refractive indexes of the
air filling the cavities of the honeycomb and that of the wet wall in the middle
stage of dehydration. There are rather well-founded objections to this explanation.
Owing to the different refractivity of the dry wall and the air, a dried-out gel
should appear completely white and opaque, for instance like kaolin, which has a
similar structure.

We may postulate a state of the gel in which water and water vapor is nonuni-
formly distributed in it. In this case, the appearance of turbidity should be ob-
served, depending on the difference between the refractive indices of the vapor
and liquid.

By assuming such a distribution of liquid water and water vapor in the gel, the fact that the Z curve in Fig. 34 lies above the A curve may be explained. It was thought previously that the cells of the gel undergo deformation when it is dried, and that this deformation is not eliminated by a new hydration, so that a higher pressure is now required to fill the cells to their former state of filling. Together with this explanation, which is probably true in part, there is another factor that enters into the situation. The liquid meniscus formed when the liquid rises (path Z) in an unwetted capillary tube is more curved than the meniscus formed by the liquid on the reverse path in the wetted capillary (path A). The pressure necessary to form a curved meniscus is higher than that required to form a more planar meniscus.

In addition to the capillary lowering of the vapor pressure on the formation of the meniscus, there is also undoubtedly an effect of the lowering of vapor pressure due to the formation of a hydrogen bond between the hydrogen of the water and the oxygen of the gel, as well as that due to adsorption of the water.

Water Glass

The preparation of pure silicates from aqueous solutions is impossible, owing to the extremely weak acid character of the polysilicic acids, as well as their tendency to form colloidal solutions and to precipitate out of these solutions in the form of gels. Fresh silicic acid gels readily dissolve in alkali to form silicates (Bibl. 21).

Alkaline salts may be prepared by fusing silicon dioxide with alkalies or carbonates, but in this case the carbonic acid is only partially displaced from the carbonates if no measures are taken to remove it from the surrounding atmosphere; but deep decomposition already takes place when these melts are treated with water. Such a fused silicate (soluble glass) was first prepared by Van Helmont in the 17th century. Another method is used today to prepare water glass, or soluble glass.

Preparation of water glass, or soluble glass. A mixture of 150 g of white sand,
100 g of soda, and 3 g of charcoal is ignited at a high temperature. The mass so obtained is leached with water, forming a heavy syrupy liquid with a strongly alkaline reaction. To purify it in the laboratory, the water glass may be precipitated from the aqueous solution and again dissolved in water. This operation is repeated until the required degree of purity has been attained.

Table 84
Composition and Properties of Specimens of Water Glass

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c)</th>
<th>d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>Na₂O</td>
<td>SiO₂</td>
<td>Na₂O</td>
</tr>
<tr>
<td>1.235</td>
<td>4.2</td>
<td>4.06</td>
<td>26.8</td>
</tr>
<tr>
<td>1.325</td>
<td>4.8</td>
<td>4.68</td>
<td>31.4</td>
</tr>
<tr>
<td>1.375</td>
<td>5.0</td>
<td>2.92</td>
<td>35.5</td>
</tr>
<tr>
<td>1.39</td>
<td>4.8</td>
<td>3.21</td>
<td>38.4</td>
</tr>
<tr>
<td>1.42</td>
<td>4.5</td>
<td>3.21</td>
<td>40.0</td>
</tr>
<tr>
<td>1.5</td>
<td>2.9</td>
<td>2.82</td>
<td>44.5</td>
</tr>
<tr>
<td>1.56</td>
<td>2.5</td>
<td>2.38</td>
<td>46.7</td>
</tr>
<tr>
<td>1.6</td>
<td>2.0</td>
<td>1.95</td>
<td>48.7</td>
</tr>
<tr>
<td>1.7</td>
<td>1.6</td>
<td>1.65</td>
<td>54.5</td>
</tr>
</tbody>
</table>

a) Specific gravity; b) molar ratio; c) weight ratio; d) Concentration of solution in % by weight.

Table 84 gives the composition and properties of a few technical samples of water glass.

It will be seen from this table that the composition of water glass does not correspond to the formula Na₂SiO₃ by which it is usually arbitrarily designated.

It is hardly possible to speak of a formula for water glass at all. The idea that it is a colloidal solution of silicic acid peptized by caustic alkali would probably be more accurate.

On standing, water glass gradually absorbs carbon dioxide from the air and forms a silicic acid gel. The deposition of the gel also takes place on neutralization with acids, on addition of salts like NH₄Cl, etc.

When long heated with water, water glass may be completely dissolved, but its solution will contain mainly silicic acid peptized by alkali, together with free alkali. Even under the action of carbon dioxide, water glass is completely decomposed, and silicic acid is thrown down. When subjected to the action of heavy metals, very voluminous slimy precipitates are thrown down, containing silicic acid and the heavy metal; but the question as to how far these precipitates really do
consist of heavy-metal silicates instead of a mixture of gels of silicic acid and heavy-metal hydroxide has not as yet been investigated.

**Carborundum**

Carborundum is a compound of silicon and carbon. It may serve as an example, to some extent, of the stability of the Si-C bond.

The formation of silicon carbide by the reaction between silicon and carbon has been described in a number of papers (Bibl.22). It acquired practical importance, however, only after it was prepared by Arecon in 1890 in an attempt to crystallize carbon by dissolving it in aluminum silicate on heating it in an electric arc furnace. The product obtained was called carborundum, since it was considered to be a compound of carbon and aluminum. The product was only found later to be similar in physical and chemical properties to silicon carbide. A number of patents were taken out on the preparation of carborundum, and based on them the industrial production of this extremely important artificial abrasive was commenced (Bibl.23).

Silicon carbide was discovered in nature by Loissan in 1904-1905, who found it in an iron meteorite, separating about 1.0 g of insoluble residue from a block weighing 183 kg by treating it with various acids. In this residue he found transparent and black diamonds, graphite, and, finally, green hexagonal crystals identical with carborundum.

Mixtures of bromoform (sp.gr.2.9) and methyl iodide (sp.gr.3.1) were used to isolate the silicon carbide (Bibl.24). The crystals floated in a mixture of sp.gr.3.2, and sank in a mixture of sp.gr.3; they did not burn in a stream of oxygen at 1000°C.

Although silicon combines with carbon at a temperature as low as 1200°C, forming an amorphous green powder of silicon carbide, crystalline carborundum is formed only at 1950°C, while it dissociates at 2200°C. The possibility of slow formation of carborundum at lower temperatures, however, is still not excluded (Bibl.25). There are references to the formation of carborundum at a temperature as low as
Carborundum in the form of light green crystals was obtained by the reaction of carbon and silicon vapors in an electric arc (Bibl.26).

As an example of an industrial method of producing carborundum, a method that did not differ fundamentally from the modern methods may be given (Bibl.27).

Preparation of carborundum. Carborundum is prepared in furnaces built of refractory brick (dimensions 3 x 1.5 x 1.5 m). The short walls are 60 cm thick and carry electrodes each consisting of 60 carbon rods (size of the rods, 75 x 750 mm), connected with the feed wires through copper caps fitting into the openings of square copper plates attached by bolts to the outside of the walls. Only the two short walls and the sole of the furnace are stationary, while the side walls are put up after charging and taken down to remove the product.

During charging, the furnace is half filled with the materials, which must not come in contact with the electrodes; a cylindrical core about 5½ cm thick is then built up of pieces of coke, 12-18 mm in size, between the electrodes, and the charging of the furnace to a height of 2½ m is completed. The electric current passing through the coke forms numerous arcs producing a very high temperature. The percentage composition of the charge is as follows:

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Coke</td>
<td>3½.2</td>
<td>Sawdust</td>
</tr>
<tr>
<td>Sand</td>
<td>5½.2</td>
<td>Salt</td>
</tr>
</tbody>
</table>

The salt is used as a flux. The sawdust increases the porosity, thus facilitating the emission of the carbon monoxide formed by the reaction

\[
\text{SiO}_2 + 2\text{C} \rightarrow \text{Si} + 2\text{CO}
\]

About 6 tons of carbon monoxide are evolved from a single charge, and is burned above the furnace.

The carborundum is taken out in the form of large blocks, which are first bro-
Len up and washed with water in a crusher, then heated with sulfuric acid (1: 2) for 3 days at 100°C, and then washed again with water. The carborundum is sized by means of screens and the finest sizes by elutriation.

When carborundum is produced in furnaces similar to those we have just described, a layer of soft graphite is formed around the core. Next comes a layer of crystalline carborundum, and, last of all, a layer of amorphous carbide.

Pure carborundum is colorless, the best technical grades are light green, while the less pure grades are black. The crystals are most often hexagonal plates. The structure of the crystal lattice of carborundum is similar to that of the diamond, but half the total number of carbon atoms in it have been replaced by silicon atoms. The interatomic distance Si - C is 1.90 Å.

The specific gravity of carborundum ranges from 3.1716 to 3.211, depending on the content of impurities, mainly of iron silicide. The Mohs hardness of carborundum is about 9.5, higher than that of corundum, but lower than the hardness of the diamond. Diamond scratches carborundum, but carborundum scratches certain varieties of the diamond.

The electrical conductivity of carborundum is low at ordinary temperatures, but rises rapidly on heating. It has no magnetic properties.

Carborundum possesses very high chemical resistance. According to Kossen, hydrogen, nitrogen, and carbon monoxide do not act on carborundum; oxygen up to 1000°C likewise has no effect on carborundum; air begins to oxidize it between 1000°C and 1350°C. Water vapor and carbon dioxide act only at their dissociation temperatures, at 1775-1800°C. The action of chlorine at 600°C is superficial, while complete decomposition takes place at 1200°C. Up to 900°C, SiCl₄ and elementary hydrogen are formed, and at 1000-1100°C CCl₄ is also formed. The vapor of NaCl does not act on carborundum up to 1000°C.

Boiling hydrochloric, sulfuric or hydrofluoric acids, or a mixture of nitric and hydrofluoric acids, all fail to act on carborundum, but phosphoric acid of
sp.gr.1.75, on heating to 230°C for 3 hours, converts it into a gel (Bibl.28).

When silica is fused with carborundum at 2000-2500°C, elementary silicon is formed (Bibl.29):

\[ 2SiC + SiO_2 \rightarrow 3Si + 2CO \]

Carborundum forms metallic silicides: with copper oxide at 800°C, with iron or nickel oxide at 1300°C, with manganese oxide at 1360°C, and with chromium oxide at 1370°C.

Fused caustic alkalies, carbonates, alkali-metal sulfates, borax, calcium or magnesium oxide, and cryolite, at 1000°C, decompose carborundum; sodium silicate and lead chromate act similarly. Potassium chlorate and nitrate, on the other hand, have no perceptible action on carborundum when fused with it.

HIGH-MOLECULAR ORGANOSILICON COMPOUNDS

The study of high-molecular organosilicon compounds is rather complicated, owing to the difficulty of isolating them in the chemically pure state.

The composition and structure of polymers must very often be judged on the basis of a study of the chemical processes leading to their formation, and of the physico-chemical properties of the polymers.

Present views on the mechanism of hydrolysis and condensation of the hydrolysis products are completely established with respect to the esters of orthosilicic acid, the halosilanes, the alkyl-(aryl)-chlorosilanes, and the alkyl-(aryl)-substituted esters of orthosilicic acid, provided these processes take place with insufficient water. These processes have been discussed in the relevant Chapters. In this Chapter we shall present considerations on the general principles of the mechanism of the processes of formation of organosilicon resins, elastomers, and other products.

Resins and elastomers are formed during the process of hydrolysis or cohydrolysis of monomeric organosilicon compounds, with an excess of water, followed by con-
version of the hydrolysis products into high-molecular substances by heating or the action of catalysts. As a result of these processes the composition of the reacting molecules is modified; when the monomeric molecules interact, water or some other substance is given off, and complex compounds are formed.

The most convenient method of studying the processes that take place on the formation of polyorganosiloxanes during the hydrolysis of alkyl-(aryl)-chlorosilanes or substituted esters of orthosilicic acid is to conduct the hydrolysis by the action of water in a quantity insufficient to complete the reaction. This method, first used in 1938 to study the mechanism of hydrolysis of alkyltriethoxysilanes (Bibl.30), and later for dialkyldiethoxysilanes (Bibl.31), has enabled us to establish the fact that when an organosilicon compound reacts with an insufficient quantity of water, the following reaction takes place at the initial instant:

\[
\begin{align*}
R \ XSi/X &+ RH \rightarrow R \ S, i R' /X OH \\
\end{align*}
\]

where \( R \) = a radical \\
\( R' \) = a radical, alkoxy or other group;  \\
\( X \) = a functional group (alkoxy group or halogen).

The hydrolysis is accompanied by immediate condensation, forming the siloxane bond:

\[
\begin{align*}
RR' \ XSiOH + HOSiRR' \rightarrow RR' \ XSi-O-SiXRR' + H_2O \\
\end{align*}
\]

Continuation of the process of partial hydrolysis and stepwise condensation leads to the formation of a polyorganosiloxane of predominantly linear structure:

\[
\begin{align*}
RR' \ XSiOSiRR' + H_2O \rightarrow RR' \ XSiOSiRR' - OH + HX \\
2RR' \ XSiOSiRR' OH + HOSiXRR' \rightarrow RR' \ XSiOSiOSiRR' X + H_2O
\end{align*}
\]
etc. The reaction product of the partial hydrolysis is a mixture of polyorganosiloxanes, homologous polymers of the general formula $X(RR'SiO)_xSiRR'X$, terminated by functional groups.

This mechanism of the partial hydrolysis of dialkylidiethoxysilanes and alkyltriethoxysilanes has been completely confirmed by investigations of the process of hydrolysis of dimethyldiethoxysilane and methyltriethoxysilane (Bibl.32), and also of dimethyldichlorosilane (Bibl.33), $SiCl_4$ (Bibl.34), and orthosilicic acid esters (Bibl.35). When 1 mol of dimethyldiethoxysilane reacts with 0.75 mol of water in an alkaline medium, the reaction product is a mixture of polydimethylsiloxanes of the general formula

$$C_2H_5O[Si(CH_3)O]_xC_2H_5$$

The functional groups in the products of partial hydrolysis retain their chemical nature. For example, the chlorine atom, under the action of ethylene oxide, readily forms chloroethoxy group.

$$Cl(\text{SiR}O)\text{SiR}Cl + 2CH_2CH_2O \rightarrow Cl\text{CH}_2\text{CH}_2O(\text{SiR}O)\text{SiR}O\text{CH}_2\text{CH}_2Cl$$

like the corresponding reaction of the alkylchlorosilanes, the process proceeds to completion at a temperature of 50-60°C.

A study of the velocity and thermal effect of the reaction of hydrolysis with excess of water enabled me to establish (Bibl.36) that, in contrast to hydrolysis in a nonaqueous medium by insufficient water, leading to the reactions of partial hydrolysis and stepwise condensation, complete hydrolysis takes place at the very beginning of the process, with hydrolysis by an excess of water, and is accompanied by almost simultaneous formation of all the hydroxyls.

Comparison of the properties of various classes of organic and organosilicon compounds containing oxygen shows that such organosilicon compounds are distinguish-
ed by an incomparably greater tendency to polymerization. While the aldehydes, $\text{RC}_2\text{OH}$, and the ketones, $\text{RC}_2\text{O}$ are substances that are completely stable in the monomeric form, the corresponding organosilicon compounds, $\text{RSiO}_2$ and $\text{R}_2\text{SiO}$ have not yet been isolated in the monomeric form, but are well known in the form of elementary units (structural units) of the molecular chains of polyorganosiloxanes.

Study of mass-spectrograms obtained in the analysis of the cleavage products of octamethyloctetrasiloxane ($\text{CH}_3\text{SiO}_4$) and of a polydimethylsiloxane elastomer has established the formation, in the ionization chamber of the mass spectrometer, of considerable quantities of dimethylsilicone ($\text{CH}_3\text{SiO}^+$) and its dimer $[\text{CH}_3\text{SiO}]_2^+$. This was the first confirmation of their existence. Without mentioning all the fragments so obtained, I shall point out only those that characterize the cleavage of the siloxane bond of the polymer. Their quantities are given in percent of the total quantity of cleavage products obtained in the given experiment.

<table>
<thead>
<tr>
<th>Compounds isolated on analysis of cleavage products of tetramer</th>
<th>Content in percent of total cleavage products</th>
</tr>
</thead>
<tbody>
<tr>
<td>($\text{CH}_3\text{SiO}^+$)</td>
<td>5.6</td>
</tr>
<tr>
<td>$[\text{CH}_3\text{SiO}_4]^+$</td>
<td>5.2</td>
</tr>
<tr>
<td>$[\text{CH}_3\text{SiO}]_2^+$</td>
<td>5.8</td>
</tr>
<tr>
<td>$[\text{CH}_3\text{SiO}]_4^+$</td>
<td>6.2</td>
</tr>
</tbody>
</table>

Fragments of the tetramer, in various stages of dehydrogenation, were also found.

The polydimethylsiloxane elastomer was taken in two forms: in its original state and in the form of a vulcanized resin with $\text{TiO}_2$ as a filler. A study of the resin on the mass spectrometer established the presence of the following compounds:
Analysis of the original elastomer gave about the same picture. Consequently the cleavage of the tetramer and the elastomer proceeds by the elementary units of the main structural unit of the polymer chain. From 1 to 4 members are detached in the elastomer. Three and four members immediately combine into a ring to form the trimer and tetramer, and in the ionization chamber they are deprived of the methyl radicals.

On the mass-spectrographic analysis, at 200°C, of a polydimethylphenylsiloxane resin whose molecules consist of the units:

\[
\text{CH}_3 \quad \text{Si} \quad \text{O} \quad \text{Si} \quad \text{O} \quad \text{Si} \quad \text{O} \quad \text{Si} \quad \text{O} \quad \text{Si}
\]

I was able to detect the following particles (Bibl.37):

\[
\begin{align*}
(CH_3)_3SiO^+ & \quad 4.2 \\
C_6H_5SiO_2^+ & \quad 4.6
\end{align*}
\]

On cleavage of polydiethylsiloxane, diethylsilanone, \((C_2H_5)_2SiO^+\), is formed; on cleavage of polydibutylsiloxane, dibutylsilanone, \((C_4H_9)_2SiO^+\); on cleavage of diamylsiloxane, diamylsilanone, \((C_5H_{11})_2SiO^+\).

The hydroxyl derivatives of carbon, containing a single OH group attached to the carbon atom, for instance the alcohols, are stable substances. The corresponding organosilicon compounds, the silanols (for instance, the trialkylsilanols), are,
in contrast, unstable compounds, and often condense into siloxanes at the very instant of their formation.

It has not been possible to prepare compounds with two OH groups attached to a single carbon atom, since aldehydes or ketones are formed instead.

Silicon, in contrast to carbon, is able to hold two hydroxyl groups or more, as is confirmed by the existence of orthosilicic acid, Si(OH)$_4$, in aqueous solutions (Bibl.8), and still more by the preparation of dialkyl-(diaryl)-silanediols, as well as that of phenylsilanetriol and dichlorophenylsilanetriol in the free state. The cleavage of water from the molecules of the dialkyl-(diaryl)-siloxanes, in contrast to organic compounds, results in the formation, not of monomeric products but of polymeric ones, the polyorganosiloxanes.

Organic compounds with three hydroxyl groups attached to a single carbon atom split off water to form organic monomeric acids RCOOH (chloral hydrate, $\text{C}_3\text{Cl}_2\text{CC(OH)}_3$, is an exception). The alkyltrisilanols possess a tendency still greater (than the mono- and dihydroxy compounds) to form complex polymeric molecules.

Taking account of the formation of dialkylsilanones and RSiO$^+$ particles observed on the cleavage of polyorganosiloxanes, and also taking account of other experimental data, the following basic hypotheses may be advanced, defining the mechanism of the process of complete hydrolysis of organosilicon compounds and of their conversion into high-molecular products.

The RR'SiXOH (cf. Reaction (1)) formed at the initial instant of the hydrolysis of a dialkylhalodisilane, a dialkylchlorohydroxysilane, or a dialkylalkoxyhydroxy-silane, may then react either according to the pattern of stepwise condensation (2) or according to the pattern of complete hydrolysis (5):

$$\text{RR'SiXOH} + \text{H}_2\text{O} \rightarrow \text{RR'Si(OH)}_3 + \text{HX}$$  \hspace{1cm} (5)

The unstable intermediate product of the reaction, the dialkylsilanol, is capable of entering into a reaction of stepwise intermolecular condensation to form a
linear dihydroxypolyorganosiloxane:

\[
2RRSi(OH)_2 \rightarrow RRSi(OH)\rightarrow OSiRR(OH) + H_2O
\]

or the reaction of intramolecular dehydration:

\[
RRSi(OH)_2 \rightarrow RRSi=O + H_2O
\]

The unstable monomer formed is immediately polymerized, giving a mixture of cyclic low-molecular or high-molecular polydialkylsiloxanes:

\[
xRRSi=O \rightarrow (RRSi=O)_x
\]

Thus there may in fact be two competing directions for the reaction:

A. Stepwise condensation of the products of complete or incomplete hydrolysis, leading to the formation of polymers of linear structure (cf. Reactions (2) to (6)).

B. Intramolecular dehydration of the products of complete hydrolysis, forming unstable monomeric dialkyl-(diaryl)-silanones, which polymerize immediately, giving a mixture of cyclic low-molecular and high-molecular polyorganosiloxanes (cf. Reactions (7) and (8)).

Under the conditions of partial hydrolysis, as a rule, the reaction proceeds only according to scheme A. With complete hydrolysis, both competing directions A and B take place, and, according to the conditions, the reaction may be directed mainly either by pattern A, in which case the cyclization is held to a minimum, or mainly by pattern B, in which case the products will be predominantly cyclic polymers. Examples to illustrate the influence of the reaction conditions on the predominance of one of these patterns or the other will be discussed in detail below. The experimental data on the hydrolysis of various organosilicon compounds are in agreement with this system, although the definitive elucidation of the mechanism of
the process does involve a number of serious difficulties, due to the exceptional activity of monomeric organosilicon oxygen-containing compounds in the reactions of condensation and polymerization.

There are two facts that confirm the view that the process of formation of high-polymer organosilicon compounds includes not only reactions of condensation but also reactions of polymerization.

On the hydrolysis of trifunctional organosilicon monomers in a strongly acid medium, in the presence of a solvent, the formation of polymers with rings in their structure is observed. The possibility of the formation of cross-linked polymer molecules from cyclic polymer molecules depends on the size of the organic radical. With increasing size of the organic radical, the predominance of intramolecular condensation is observed, owing to the steric hindrance connected with the large dimensions of the organic radical. The reaction of hydrolysis and condensation of trifunctional monomers may be represented as follows:

\[
\text{RSiCl}_3 + H_2O \rightarrow \text{RSi(OH)}_3 \quad \text{polymORIZATION} \rightarrow \quad (\text{RSi(OH)})_n \quad \text{condensation} \rightarrow
\]

A polymeric molecule with hydroxyl groups in its cyclic units is capable of the reactions both of intramolecular and intermolecular condensation with cleavage of water. In the former case, with the intramolecular cleavage of water, the transition of the polymer to an infusible, insoluble state should be observed.

The predominance of one or the other of these reactions largely depends on the size of the organic radical attached to the silicon atom. In the case of an aromatic nucleus, which creates steric hindrance to intermolecular condensation, the rate of
transition of the polymer into an infusible, insoluble state will be slowed. This explanation is confirmed by the fact that polymethylsiloxane resins pass over considerably faster into an infusible, insoluble state than polyphenylsiloxane resins of the same functionality, and prepared under identical conditions.

Thus, on the hydrolysis of trifunctional compounds in an acid medium, in the presence of indifferent solvents, we observe the formation of polymer chains containing rings.

When high-molecular polyorganosiloxanes are heated to 400°C, processes of thermal rearrangement take place: the siloxane chain of the polymer molecule is broken down, and volatile low-molecular polydialkyl-(aryl)-siloxanes are liberated, mainly trisiloxane \( (R_3SiO)_3 \). The composition of the structural unit is preserved, and thus we have here a typical process of depolymerization.

The reaction of depolymerization has been investigated on the example of polydimethylsiloxane, prepared by hydrolysis of dimethyldichlorosilane and followed by distillation to remove the volatile low-molecular polymers (Bibl.33), and also on the example of polydiphenylsiloxane (in the latter case the process was run in vacuo, and the hexaphenyltrisiloxane was distilled off).

The reaction of depolymerization of polymethylsiloxane prepared by hydrolysis of methylidichlorosilane, \( CH_3SiHCl_2 \), has recently been described. The reaction product is trimethylhydroxycyclotrisiloxane, \( (CH_3SiHO)_3 \).

In the presence of a 1% solution of alkali at 300°C, the depolymerization reaction of a polyorganosiloxane consisting of mono- and bifunctional structural units may likewise be conducted. In this case the reaction product is a polydialkylcyclotrisiloxane \( (RR'SiO)_x \), where \( x = 3 \) or 4.

The presence of a monomeric dimethylsilanone in the cleavage products of polydimethylsiloxane was discovered when it was heated to 250°C (under residual pressure of 10^6 mm Hg) and the reaction products were conducted to the ionization chamber of a mass spectrometer.
Taking account of the existence of a monomeric dimethylsilanone (Bibl.37), it may be assumed that on heating of a high-molecular polyorganosiloxane, its depolymerization first occurs, forming an unstable monomeric dimethylsilanone $R_2SiO$, which immediately polymerizes; thus forming a mixture of cyclcal polydialkylsiloxanes, from which the low-boiling compounds are removed from the sphere of the reaction by being distilled off, while the high-boiling compounds are again depolymerized, so that the end products of the reaction consist only of low-molecular compounds.

The existence, alongside of the condensation processes in the formation of polyorganosiloxanes, of polymerization processes as well, is confirmed by the high polydispersion of the products. On fractionation of a polydimethylsiloxane by fractional precipitation from a solution in ethyl acetate and acetone (Bibl.39), five fractions were obtained, whose molecular weights, osmometrically determined, ranged, according to Scott, from $2.9 \times 10^5$, for the second fraction, to $2.8 \times 10^6$, for the fifth. Thus the coefficient of polydispersion for the polymer as a whole exceeds 10. On fractionating a polyethylsiloxane elastomer, I obtained a distribution curve indicating a still higher degree of polydispersion (Bibl.36). According to data of A.Ya.Korolev, K.A.Andrianov, et al (Bibl.40), the polydispersion determined in a polydimethylsiloxane with the average molecular weight of 74,000, is very high. The molecular weight of individual fractions of this polymer ranged from 21,000 to 1,290,000 (Table 85).

The differential distribution curve by molecular weight is found to be strongly blurred. The ratio of the molecular weight of the highest molecular fraction to the lowest molecular fraction is 61.4. Two maxima are also observed on the differential distribution curve.

A study of the structure of linear polydimethylsiloxanes and an investigation of their molecular weight, determined viscosimetrically, osmometrically, and by the diffusion method, allowed evaluation of the degree of asymmetry of the molecule and calculation of its absolute dimensions. With increasing molecular weight of the
fraction, the degree of asymmetry of the molecules, that is, the ratio between the semiaxes of the asymmetric macromolecule, varies (Bibl.40) over the range from 9.6 to 53.2. Thus, in the polydimethylsiloxane elastomer, with increase of molecular weight from 21,000 to 1,290,000, the major axis of the macro-increases 12.3 times, while the minor axis increases only 2.2 times. This shows that the increasing molecular weight of the fraction is connected with the increased degree of asymmetry, and, consequently, with the growth of the molecules primarily along the long axis.

Rochow (Bibl.41) made an electron-microscope study of the molecular weight of a polydimethylsiloxane elastomer (under 100,000 enlargement) and concluded that the molecules were large. But these data of Rochow cannot be considered entirely reliable, owing to the blurring of the boundaries of the observed particles and the difficulty of precisely determining their actual dimensions from the micrograms obtained.

It has been noted in the literature (Bibl.42) that the coefficient of polydispersion for rubbers amounts to 5 - 7, but that it is considerably less for condensation polymers. For organosiloxanes, formed by a combined polymerization-condensation process, a high degree of polydispersion is a natural consequence of the two reactions proceeding simultaneously.

The data we have presented confirm the correctness of our hypothesis that polymerization reactions play a substantial role in the formation of polyorganosiloxanes, alongside of condensation reactions.

Let us consider the conditions influencing the predominant direction of the
process in either the pattern of stepwise condensation (A) or the pattern of intramolecular dehydration and polymerization (B).

The principal factors resulting in the predominance of one or the other of these two competing reactions, are the acidity of the medium and the presence of solvents.

On the complete hydrolysis of bifunctional compounds in a neutral or alkaline medium (for alkylchlorosilanes, in the presence of higher alcohols), linear polydialkylsiloxanes of relatively high molecular weight are for the most part formed. The presence of alkoxyl groups as the end groups is characteristic for the products of hydrolysis of the substituted esters, while the presence of hydroxyl groups as end groups is characteristic for the products of hydrolysis of the alkylchlorosilanes (Bibl.3).

The yield of low-molecular cyclic polysiloxanes is low under these conditions, which is evidence of the predominance of the stepwise condensation reactions.

Such a course of the process of hydrolysis may be explained by the blocking of a certain number of functional groups by metal ions, in the presence of alkali, as follows:

\[ -O-SiR_2-OH + NaOH \rightarrow -O-SiR_2Ona + H_2O \]

and, in the case of alkylchlorosilanes, as follows:

\[ -O-SiR_2-Cl + 2NaOH \rightarrow -O-SiR_2Ona + H_2O + NaCl \]

*The possibility of blocking reactive groups by metallic ions is confirmed by the fact that on the reaction of alkyltrithoxysilanes with concentrated alkalies, compounds containing one, two or three blocked hydroxyl groups have been obtained (Bibl.36):
The grouping so formed is relatively stable, since the oxysodium group is hydrolyzed only slowly in an alkaline medium. On the hydrolysis of alkylchlorosilanes in the presence of alcohols, alkoxyl groups are similarly formed:

\[
\begin{align*}
\text{R} \quad \text{R} \\
\text{Si-Cl} + \text{R’OH} \rightarrow \text{Si-OR’} + \text{HCl}
\end{align*}
\]

which are likewise relatively stable, since the hydrolysis of the substituted esters (and in particular the completion of such hydrolysis) requires conditions considerably more drastic than those demanded by the process of complete hydrolysis of the alkylchlorosilanes.

The existence of relatively stable blocked functional groups at the instant of hydrolysis reduces the quantity of the intermediate products of complete hydrolysis, namely the dialkylsilanediols, so that the probability of the reaction of intramolecular dehydration may be considerably diminished. But the reaction of intramolecular dehydration proceeds even in these cases, since the reaction mixtures always contain cyclic polymerization products.

Thus, for instance, on hydrolysis of dimethyl dichlorosilane by 6N ammonia solution, the yield of low-molecular cyclical products is reduced to 20% (against 57% on hydrolysis in an acid medium).

The number of papers devoted to the investigation of the process of complete hydrolysis in a neutral or alkaline medium is very small, which is obviously due to the difficulty of isolating and studying the high-polymer reaction products. The most convenient approach to the consideration of this complex process is by comparing the properties of the polymers formed on hydrolysis with water in various quantities close to the theoretical. Such an investigation (very much simplified) has been performed on the hydrolysis of dimethyldiethoxysilane (Bibl.14).

Polymers prepared by the hydrolysis of dimethyldiethoxysilane by water, in
quantities from 0.921 to 1.072 mol per mol of dimethyldiethoxysilane, were fractionally distilled in vacuo to separate the volatile portion from the nonvolatile, and to investigate these portions and the quantitative relation between the characteristics of each separate portion.

The results of the work show that, with increasing quantity of water entering into the reaction, there is a decrease in the relative quantity of the volatile portion, which evidently consists of the low-molecular products of incomplete hydrolysis, and a sharp fall in the number of ethoxy groups in both volatile and nonvolatile portions, which indicates that the hydrolytic processes have on the whole been completed. The refractive index, the density, and, in particular, the molecular weight and viscosity of the nonvolatile portion of the polymer increase sharply, which indicates that the processes of condensation have on the whole been completed, and also indicates that the process of complete hydrolysis under the action of water in quantities over 1 mol obviously proceeds in the direction of the formation of linear polymers of molecular weight over 20,000, with ethoxy groups (0.5%) at the ends. The number of ethoxy groups in the volatile portion also decreases sharply, but the percentage of the volatile portion still remains rather high (12%), which points to the existence of a cyclization reaction. It may thus be concluded, on the basis of the experimental data, that the process of complete hydrolysis of dimethyldiethoxysilane in an alkaline medium proceeds primarily by Scheme (A), and that the reactions of intramolecular dehydration and polymerization (B) are of secondary importance.

The course of the process of hydrolysis in an acid medium differs substantially from the process of hydrolysis just discussed. Both in the case of the substituted esters of orthosilicic acid (hydrolysis in presence of acid), and in the case of the alkyl-(aryl)chlorosilanes (hydrolysis by water without neutralization of the HCl), the process of complete hydrolysis leads to the formation, mainly or entirely, of cyclic polydialkylsiloxanes of low molecular weight.
A number of cyclic polydiethylsiloxanes, \([\text{Si}(\text{C}_2\text{H}_5)_2\text{O}]_x\), have been detected in the products of complete hydrolysis of diethylidithoxysilane in an acid medium (Bibl.38).

When dimethyldithoxysilane is hydrolyzed by aqueous ethyl alcohol in the presence of HCl, the principal product is a mixture of cyclic dimethylsiloxanes, \([\text{Si}(\text{CH}_3)_2\text{O}]_x\); polymers with 6 to 12 silicon atoms in the ring have been isolated and studied (Bibl.115).

Various dialkyl- (diaryl)-dichlorosilanes, on hydrolysis with water (without neutralization of the HCl liberated), yield the low-molecular cyclical polysiloxanes indicated in Table 86.

<table>
<thead>
<tr>
<th>Alkylchlorosilane formula</th>
<th>Yield of cyclic polysiloxanes</th>
<th>Number of Si Atoms</th>
<th>in principal compound</th>
<th>in split-off</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{CH}_3)\text{SiCl}_2)</td>
<td>57</td>
<td>3</td>
<td>4</td>
<td>3 to 9</td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_5\text{SiCl}_2)</td>
<td>90</td>
<td>3</td>
<td>4,5 and 6</td>
<td></td>
</tr>
<tr>
<td>((\text{C}_6\text{H}_5)\text{SiCl}_2)</td>
<td>62</td>
<td>3</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_5\text{CH}_3\text{SiCl}_2)</td>
<td>78</td>
<td>3</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>(\text{C}_4\text{H}_9\text{C}_2\text{H}_5\text{SiCl}_2)</td>
<td>77.5</td>
<td>3</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>

a) Alkylchlorosilane formula; b) Yield of cyclic polysiloxanes; c) Number of Si Atoms; d) in principal compound; e) in split-off products.

It will be seen from the data presented that, on hydrolysis in an acid medium, low-molecular cyclic polyorganosiloxanes are mainly formed. We may point out that with increasing acidity of the medium the yield of low-molecular cyclic compounds increases (Bibl.33).

Thus, for example, when dimethyldichlorosilane is hydrolyzed, not by water but by 6N HCl, the yield of cyclic products increases from 57 to 73%.

As already pointed out, the presence of an inert solvent exerts a great influence on the course of the process of complete hydrolysis. Thus, when water acts on a solution of dimethyldichlorosilane in 1 to 2 parts by volume of ether, the yield of cyclic low-molecular polymers increases to 97–98%. Obviously, in the presence of an inert solvent, the individual molecules are further apart, so that the probability of effective collisions between them, and of the reaction of intermolecular condensation, diminishes. There is, accordingly, a considerable increase in the...
probability of the competing reaction of intramolecular dehydration and formation
of a monomeric dialkylsiloxane, which immediately polymerizes, mainly yielding a
mixture of cyclic polydialkylsiloxanes of low molecular weight.

In this way, the proposed mechanism of the reaction on hydrolysis in an excess
of water allows explanation of the experimental data indicating the formation of
considerable quantities of low-molecular polydialkyclosiloxanes in acid medium,
and also in the presence of inert solvents.

A combined condensation-polymerization process of conversion of organohydroxy-
silanes into polyorganosiloxanes takes place not only in bifunctional systems, but
also in systems with a higher functionality (cohydrolysis of \( R_2\text{Si}X_2 \) and \( R\text{Si}X_3 \)). As
in bifunctional systems, here, too, according to the conditions, the process may
proceed either in the direction of stepwise hydrolysis and condensation, forming
high-molecular polymers of cross-linked structure, or in the direction of the forma-
tion of cross-linked rings of lower molecular weight.

The process of formation of cross-linked polymers is extremely complicated, so
that no works devoted to the investigation of the reaction conditions of hydrolysis
and their influence on the structure of the polymer have yet been published in the
literature. It may, however, be said without doubt that the questions of the block-
ing of reactive groups by metallic ions or by alkoxy groups are of no less impor-
tance for the trifunctional compounds than for bifunctional ones, and that the prop-
erties of the hydrolysis product depend to an even greater extent on the acidity of
the medium, and, in particular, on the presence of higher alcohols during the pro-
cess of hydrolysis.

If the condensation of the hydrolysis product is conducted by heating it and
simultaneously blowing air through it, the process of formation of polyorganosilox-
anes may be still further complicated by the additional reaction of oxidation of
the organic radical, followed by formation of a siloxane bridge, cross-linking the
molecular chains:
and also by the liberation of the oxidation products of the radical (aldehydes, water, CO₂ and H₂). Reactions of this type are of great importance in the process of preparing resins, and may ultimately lead to the formation of infusible and insoluble products. For the polymethylsiloxanes, the by-products of the reaction are formaldehyde, CO and H₂, for polyethylsiloxanes, acetaldehyde, etc.

Polyorganosiloxanes may contain the same or different radicals attached to a single silicon atom:

Such polymers are prepared by hydrolysis of bifunctional compounds with the same radicals attached to a single silicon atom, in the former case, and with different radicals so attached in the latter.

Cohydrolysis may yield polymers with different radicals attached to different silicon atoms.

By the cohdrolysis of several organochlorosilanes with different radicals, polymers with an even more complex combination of units in the chain may be prepared.

In spite of the complexity of the process, and of certain peculiarities in the formation of polyorganosiloxane resins and elastomers, the similarity between their
structure and that of organic polymers and silicates must be noted.

Not only linear polymers, but cyclic and space polymers as well, have a certain similarity of structure to the polyorganosiloxanes and silicates (cf. Figs. 35, 36, 37).

Figure 35 shows models of linear molecules or organic polymers (paraffin, polyethylene), polyorganosiloxanes (liquids, elastomers, and thermoplastic resins) and silicates (water glass).

Figure 36 shows models of molecules of cyclic structure: polycyclohexane, polyorganosiloxane (liquids and resins), and siloxane (quartz).

Figure 37 shows models of molecules possessing a spatial structure: organic space polymers, thermoreactive polyorganosiloxanes, and siloxanes.

It must, however, be pointed out that the analogy between these forms of polymers is confined to the similarity in the arrangement of the atoms in the molecule alone. While in the silicates the silicon atom is located at the center of a tetrahedron whose vertices are occupied by oxygen atoms, in the polyorganosiloxanes organic radicals occupy one or two vertices of the tetrahedron, which makes deformation of the tetrahedron possible and gives flexibility to the molecule as a whole.

One of the most important properties of polyorganosiloxanes, their low viscosity-temperature dependence, may be explained by the absence of hydrogen bonds between the molecular chains (Bibl. 46), as well as by the free rotation of the structural units about the siloxane bond (Bibl. 47). Both these circumstances prevent the creation of "tight packing" of the molecules, and are responsible for the low degree of interaction between the molecules.

Free rotation of the structural units \((\text{CH}_3)_2\text{Si-O}\) has been established by X-ray study of so rigid a molecule as octamethyldicyclopentasiloxane:

\[
\begin{align*}
\text{(CH}_3)_{2}\text{Si} & \quad \text{O} \\
\text{O} & \quad \text{Si} \\
\text{Si} & \quad \text{O} \\
\text{O} & \quad \text{Si} \quad \text{CH}_3 \\
\text{(CH}_3)_{2}\text{Si} & \quad \text{O}
\end{align*}
\]
The following data were found for this molecule: angle between the ring planes 20°; Si - O distance, 1.64 Å (against 1.83 Å in the silicates). The Si - C distance is equal to the sum of the covalent radii (1.90 Å).

Fig. 35 - Structure of Linear Molecules of Polymers:
1 - Polyethylene; 2 - Polydimethyldisiloxane; 3 - Polydisodiumoxysiloxane

Fig. 36 - Structure of Cyclic Molecules of Polymers:
1 - Polycyclohexanes; 2 - Polyorganocyclo-

Fig. 37 - Structure of Spatial Molecules of Polymers:
1 - Organic Space Polymers; 2 - Polyorganosiloxanes; 3 - Siloxanes (quartz)

a) Oxygen; b) Metal

Physical Properties of Organosilicon Polymers

Organosilicon polymers have a low viscosity-temperature coefficient, and their elastic properties vary little with temperature. Thus, for instance, the variation in the viscosity of liquid linear polyorganosiloxanes is 1/50 the variation in the
viscosity of petroleum oils.

The modulus of elasticity in a polydimethylsiloxane elastomer varies by a factor of 1.8 over the temperature range 0–80°C, while that of natural rubber varies by a factor of 100 over the range 25–64°C.

Liquid polydimethylsiloxanes of viscosity from 0.65 to 1000 centistokes are compressed by 7.3–10% under a pressure of 1000 kg/cm², while hydrocarbons (for instance, dodecane) are compressed by 6.02%.

The unusual properties of linear polyorganosiloxanes are related to their chemical structure, and to the form and volume of the molecule. The fact that the volume of the silicon atom is greater than that of the carbon atom makes the organic groups attached to it more mobile and gives flexibility to the molecular chain of the polymer.

On replacement of the oxygen in organosiloxanes by other atoms or groups, the forces acting within the molecule are modified, leading to the production of compounds with different physical properties. This will be clear from Table 87.

<p>| Table 87 |
|------------------|------------------|------------------|------------------|
| Relation between the Physical Properties of Polymers of the Type |
| (CH₃)₃Si–A–Si(CH₃)₃ on their Composition and Structure |</p>
<table>
<thead>
<tr>
<th>A</th>
<th>Boiling Point °C</th>
<th>Freeze Point °C</th>
<th>Viscosity at 25°C in Centistokes</th>
<th>Activation energy of viscous flow in cal</th>
</tr>
</thead>
<tbody>
<tr>
<td>—O—</td>
<td>100</td>
<td>—67</td>
<td>0.65</td>
<td>2115</td>
</tr>
<tr>
<td>—NH—</td>
<td>114</td>
<td>13</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>—CH₃—</td>
<td>126</td>
<td>—70</td>
<td>0.89</td>
<td>2640</td>
</tr>
<tr>
<td>—S—</td>
<td>168</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>—(—) —</td>
<td>240 (approx.)</td>
<td>—88</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>—(—) —</td>
<td>240 (approx.)</td>
<td>—26</td>
<td>2.535</td>
<td>3530</td>
</tr>
<tr>
<td>—(—) —</td>
<td>240 (approx.)</td>
<td>—72</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>
The structure of the molecular chain also affects other properties. Thus, for instance, polymethylsiloxanes and polydimethylmethylenesilanes of molecular weight 1200 have a surface tension of 20.2 and 26.0 dynes/cm, respectively, at 25°C. Their electrical properties also differ (Bibl.44). This will be seen from Table 88.

The side groups affect the properties of a polymer. Table 89 gives the properties of a linear decamethyltetrasiloxane and its ethyl and chloromethyl analogs (Bibl.48).

The intermolecular forces, determined from the variation in the swelling of various polymers, and expressed in the form of density of cohesion energy, are as follows:

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Density of cohesion energy, cal/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polydimethylsiloxane elastomer</td>
<td>54</td>
</tr>
<tr>
<td>Polyisobutylene</td>
<td>60</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>62</td>
</tr>
<tr>
<td>Natural rubber</td>
<td>64</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>80</td>
</tr>
<tr>
<td>Buna No. 88</td>
<td>90</td>
</tr>
<tr>
<td>Polyvinylchloride</td>
<td>90</td>
</tr>
</tbody>
</table>

A study of the compression of films of polydimethylsiloxane polymers on water (Bibl.49) has shown that the oxygen atom attached to a silicon atom orients itself toward the water. Calculations show the volume of the structural unit \((\text{CH}_3)_2\text{SiO}\), taken arbitrarily as a parallelepiped, (Bibl.50), is 132 Å. The thickness of the film is 5.0 Å, and the area of the base of the structural unit is 22.9 Å. On compression, the film thickens to 12.7 Å. These data allow the hypothesis that the molecules of polydimethylsiloxanes have the shape of spirals, each turn of which consists of six structural units, and that the axis of the spiral is parallel to the plane of the water.
Table 88

Electrical Properties of Polydimethylsiloxanes and Polydimethylmethylenesilanes (Bibl.44)

<table>
<thead>
<tr>
<th>Name of polymer</th>
<th>Dielectric Constant $\varepsilon$</th>
<th>Tangent of dielectric loss angle $\tan\theta$ at 10 cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$2\pi f = 2$</td>
</tr>
<tr>
<td>Polydimethylsiloxanes</td>
<td>2.75</td>
<td>0.0006</td>
</tr>
<tr>
<td>Polydimethylmethylenesilanes</td>
<td>2.49</td>
<td>0.00065</td>
</tr>
</tbody>
</table>

Table 89

Physical Properties of Polymers of Various Structures (Bibl.48)

<table>
<thead>
<tr>
<th>Structure</th>
<th>Viscosity at 15% in Centistokes</th>
<th>Activation Energy of Viscous Flow in cal</th>
<th>Freeze Point in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH₃)₃Si(OSi(CH₃)₃OSi(CH₃)₃</td>
<td>1.53</td>
<td>2510</td>
<td>-78</td>
</tr>
<tr>
<td>(CH₃)₃Si(OSi(CH₃)₃OSi(CH₃)₃</td>
<td>2.35</td>
<td>2500</td>
<td>-120</td>
</tr>
<tr>
<td>(C₆H₅)₂Si(OSi(CH₃)₃OSi(CH₃)₃</td>
<td>3.5</td>
<td>3120</td>
<td>-94</td>
</tr>
<tr>
<td>(CH₃)₃Si(OSi(CH₃)₃OSi(CH₃)₃</td>
<td>3.60</td>
<td>3295</td>
<td>-77</td>
</tr>
</tbody>
</table>

Studies of polyorganosiloxane films in water, and of mono-layers of polyorganosiloxanes on glass and ceramics, have made it possible to establish that the polymer molecules are so arranged that the oxygen of the siloxane group is directed toward the glass, while the hydrocarbon radicals are oriented in the opposite direction. This explains the high marginal angle of wetting (Bibl.51) of such a surface by water (90-110°).

The orientation in cellulose fibers is probably similar (Bibl.52).

The surface tension of polyorganosiloxanes at thin air and water interfaces has been measured, and on this basis the energy of adhesion to water has been cal-
culated. Polyorganosiloxanes have an energy of adhesion to water that is close to that of the hydrocarbons (only 15% greater than that of the hydrocarbons), and they are therefore not very strongly adsorbed on a water surface. The energy of adhesion has a maximum when the polydimethylsiloxane molecule is completely adsorbed by the water and its long axis is parallel to the surface of the water. It has a minimum when some of the Si and O atoms of the molecule are no longer adsorbed by the water.

The adsorption of polydimethylsiloxanes by water is explained by the polar nature of the Si-O bond.

A very important peculiarity of polymethylsiloxane molecules is their ability, in monolayers, to coil into spirals and again to uncoil. This phenomenon may serve as a basis for explaining the low viscosity-temperature coefficient of polyorganosiloxanes, which is explained by the opposing action of two factors:

1) the decrease in viscosity with increasing temperature, owing to the increasing intermolecular distances;

2) the increase of viscosity with increasing temperature, owing to the lengthening of the spiral polyorganosiloxane molecule.

The former effect is observed in all liquids, while the latter is manifested only in long, chainlike molecules, free from steric hindrances to coiling.

The methyl-substituted polysiloxanes have a greater tendency to coil than all other substituted polysiloxanes. The ethyl derivatives have this property to a lesser degree.

The high viscosity of the organosiloxanes is connected with the tendency of their molecules to coil into spirals, owing to the relatively large size of the silicon atom, as a result of which the free rotation of the chains and substituent groups is facilitated. The absence of this capability in the hydrocarbons is explained by the small size of the carbon atom by comparison with the silicon atom.

The thermal stability of the polyorganosiloxanes and their resistance to oxidation depends to a considerable extent on the organic radical. The presence of the
phenyl group increases the thermal stability of the polymer at high temperatures and to the action of atmospheric oxygen. This will be seen from Table 90, which gives the thermal stability of polydimethylsiloxane and polyphenylmethylsiloxane.

Table 90

Behavior of Polydimethylsiloxanes and Polyphenylmethylsiloxanes on Heating

<table>
<thead>
<tr>
<th>Name of polymer</th>
<th>Duration of oxidation in hrs</th>
<th>Temperature °C</th>
<th>HCOOH</th>
<th>HCHO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polydimethylsiloxane</td>
<td>168</td>
<td>200</td>
<td>17</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>225</td>
<td>8</td>
<td>22</td>
</tr>
<tr>
<td>Polyphenylmethylsiloxane</td>
<td>168</td>
<td>200</td>
<td>3</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>168</td>
<td>225</td>
<td>14</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>168</td>
<td>275</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>300</td>
<td>18</td>
<td></td>
</tr>
</tbody>
</table>

Spectral studies in the infrared region show that only the methyl groups are oxidised (Bibl. 53).

To explain the properties of the polyorganosiloxanes, an analogy may be drawn between their structure and that of quartz or silicates. While in the chain-form metasilicates we have the fibrous structure of asbestos, the low viscosity-temperature coefficient in organosiloxane polymers is explained by the very small intermolecular forces by which the interaction between the molecular chains is effected. In silicates, owing to the cross-linking, we observe the laminar structure of mica; while the polyorganosiloxanes of analogous structure constitute disordered systems, resins.

In the molecular chains of mica, feldspars and glasses, the silicon is partly replaced by aluminum, titanium, and other metals, and in glasses, frequently by boron, phosphorus, etc., as well. It is well known that the quality of glass depends on the elements of which its molecule is composed.

In one of my papers (Bibl. 54) I pointed out, for the first time, the possibil-
ity of the synthetic introduction of other elements, such as titanium, aluminum, magnesium, boron, etc. into the molecular chain of the polyorganosiloxanes. In this case polymeric compounds are obtained with molecular chains - Si - O - M - O - Si - O -, where M is the metal Al, Ti, Mg, B, etc.

This new class of polymeric compounds, termed "organosilicates" or polyorganometallosiloxanes, is of great theoretical interest.

The partial substitution of silicon in organosiloxanes by its analog germanium is theoretically interesting. But it will be possible only when we succeed in bringing an alkylchlorogermanium into the reaction of cohydrolysis with organochlorosilanes. The silicon in the polymer chain may be partially replaced by boron, but in this connection it must be borne in mind that in boron the fourth coordination bond, to which another substituent can be attached, is free. Boron forms a bond with groups amenable to hydrolysis.

A substance has recently been prepared which was isolated in the form of an intermediate compound on preparation of polydimethylsiloxane, in the presence of BF₃ as a polymerization catalyst. This new compound was also formed from trimethylthiosiloxane under the action of boric acid in the presence of an acid esterification catalyst (p-toluenesulfonic acid). It boils at 90°C and has the following structure (Bibl.55):

\[
\begin{align*}
&(CH₃)₃Si-O-B-O-Si(CH₃)₃ \\
&\quad O-Si(CH₃)₃
\end{align*}
\]

It was found subsequently that phenylboric acid and a solution of trimethylbromosilane in heptane at 96°C form phenylboroxide; the water split off during this intramolecular condensation then acts on more triethylbromosilane, forming triethylsilanol and HBr. At 140°C, in addition, a small quantity of a viscous colorless oil containing boron is also formed. The following structure is attributed to it (Bibl.56):

F-TS-9191/V 744
The introduction of metals into polymers prepared from esters of orthosilicic acid has also been described, but their composition has not yet been established (Bibl.57).

Interesting observations have been made in a study of the effect of ferric chloride on dimethylsiloxane polymers under action of ultraviolet rays. It was found that under the action of ultraviolet light and ferric chloride (Bibl.58) the \(-\text{Si}-\text{O}-\text{Si}-\) bond is broken.

It has been established that ferric chloride, like sulfuric acid and its salts, breaks down cyclic polyorganosiloxanes and converts them into linear ones. Ferric chloride may therefore be used as a catalyst encouraging the conversion of cyclic polymers into linear polymers and the formation of cross-linked polyorganosiloxanes (Bibl.59).

Cobalt, manganese, zinc, lead, calcium siccatives and others have been described as catalysts for hardening the polyorganosiloxanes (Bibl.60).

**Polymeric Organosilicon Liquids**

Organosilicon polymeric products may be obtained in the form of liquids transparent as water; they are chemically inert and resist heat and oxidation (Bibl.61).

Liquid polyorganosiloxanes consist of molecules of either linear or cyclic structure. On hydrolysis of a mixture of dialkyl dichlorosilanes and trialkylchlorosilanes, followed by condensation of the hydrolysis products, linear polymers are formed:

\[
\begin{align*}
R_2Si(OH)_2 + 2R_3SiOH & \quad \rightarrow R-Si-&-R-[-O-Si-]^{(x+1)}(R_3SiO)_{x+1}
\end{align*}
\]

F-TS-9191/V 745
The value of $x$, that is, the degree of polymerization of the product, depends on the condensation conditions and on the proportions of the reagents. An increase in the quantity of trialkylsilanol in the reaction leads to a decrease in the value of $x$, since a trialkylsilanol encourages the breaking off of the molecular chains. At the molar ratio of 5:2 between dialkylsilanol and trialkylsilanol, $x = 5$; at the ratio of 10:2, $x = 10$, etc.

In an acid medium, cyclic polymers are mainly formed, according to the reaction:

$$3R_3Si(OH)_3 \rightarrow \frac{3H_2O}{R_3SiSiR_3}$$

The number of silicon atoms in the rings may vary, depending on the reaction conditions. The cyclic polyorganosiloxanes entering into the composition of the liquid polymers may have 10 silicon atoms or more in the ring.

Liquid polysiloxanes may also be prepared by hydrolysis of the dialkyl- and trialkyl-substituted esters of orthosilicic acid. When the hydrolysis is run with insufficient water in the absence of an acid, liquid polymers containing alkoxy groups are obtained. The reaction of formation of liquid polymers under these conditions may be represented in the following general form: (Bibl.62):

$$nR_2Si(OR')_2 + \frac{1}{2}H_2O \rightarrow R'\text{OSi--O-Si--OR} + R'\text{OH}$$

In this case the quantity of water is the factor controlling the growth of the molecular chains.

Polysiloxane liquids are odorless. Their viscosities, boiling points, and freezing points vary within wide limits. These properties, and their other physical
properties, depend on the degree of condensation and on the size of the organic radical entering into the composition of the polymer molecule.

**Polymethylsiloxane Liquids**

On hydrolysis of a mixture of dimethyldichlorosilane and trimethylchlorosilane, liquid products that readily distill under reduced pressure are obtained. They are colorless liquids with low boiling points, insoluble in water and aliphatic alcohols, but soluble in aromatic hydrocarbons, dichloroethane, an ethanol-benzene mixture, etc. They are chemically inert and do not dissolve natural or synthetic rubbers, plastics, etc. Polymethylsiloxane liquids not containing ethoxy groups are prepared from a mixture of dimethyldiethoxysilane and methyltrimethoxysilane by pouring a mixture of 0.9 mol of dimethyldiethoxysilane and 0.1 mol of methyltrimethoxysilane into half its volume of 2N HCl at a temperature not over 45°C. The product, after hydrolysis, has a low viscosity, but after carbon dioxide gas is blown through it, and it has been boiled with conc. alcoholic HCl, its viscosity rises. If not over 10% of methyltrimethoxysilane is taken for the hydrolysis, the gelation of the hydrolysis product will not take place on heating to 100°C for 600 hours. The freezing point of the product is -84°C.

A number of liquid polymethylsiloxane polymers have been prepared. Table 91 gives their properties.

---

**Table 91**

<table>
<thead>
<tr>
<th>Degree of polymerisation</th>
<th>Constant at 1000 cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>a) Temperature, °C; b) Dielectric constant</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td>8</td>
<td>9</td>
</tr>
<tr>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>11</td>
</tr>
</tbody>
</table>

**Fig.38** - Relation between Dielectric Constant of Polydimethylsiloxanes of Various Degrees of Polymerisation and the Temperature

Degree of polymerisation: 1 - polymerisation 0; 2-1; 3-2; 4-3; 5-4; 6-5; 7-6; 8-7; 9-8; 10-151; 11-polymerisation 356

a) Temperature, °C; b) Dielectric constant at 1000 cycles
Table 91

Properties of Polymethylsiloxane Liquids

<table>
<thead>
<tr>
<th>Viscosity of 110°C</th>
<th>Freeze Point 0°C</th>
<th>Boiling Point °C</th>
<th>Flash Point °C</th>
<th>Spec. Gravity at 25°C</th>
<th>Coefficient of Expansion 0°C to 100°C (Kx 1000)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.65</td>
<td>-58</td>
<td>99.5</td>
<td>-1.1</td>
<td>0.761</td>
<td>1.598</td>
</tr>
<tr>
<td>1.0</td>
<td>-38</td>
<td>152</td>
<td>37.8</td>
<td>0.818</td>
<td>1.451</td>
</tr>
<tr>
<td>1.5</td>
<td>-78</td>
<td>192</td>
<td>71.1</td>
<td>0.852</td>
<td>1.312</td>
</tr>
<tr>
<td>2.0</td>
<td>-84</td>
<td>230</td>
<td>90.6</td>
<td>0.871</td>
<td>1.247</td>
</tr>
<tr>
<td>3.0</td>
<td>-70</td>
<td>70-100 (0.5 mm)</td>
<td>107.2</td>
<td>0.896</td>
<td>1.170</td>
</tr>
<tr>
<td>5.0</td>
<td>-70</td>
<td>120-160 (0.5 mm)</td>
<td>132.2</td>
<td>0.918</td>
<td>1.095</td>
</tr>
<tr>
<td>10</td>
<td>-67</td>
<td>200 (0.5 mm)</td>
<td>176.7</td>
<td>0.940</td>
<td>1.035</td>
</tr>
<tr>
<td>20</td>
<td>-60</td>
<td>220 (0.5 mm)</td>
<td>271.7</td>
<td>0.950</td>
<td>1.025</td>
</tr>
<tr>
<td>50</td>
<td>-55</td>
<td>250 (0.5 mm)</td>
<td>232.2</td>
<td>0.955</td>
<td>1.000</td>
</tr>
</tbody>
</table>

The physical and electrical properties of these polymers have been studied. The dielectric constant has been determined for a number of linear polymers containing 24, 48, 151 and 356 silicon atoms in the chain. These determinations have shown that the dielectric constant at 1000 cycles ranges from 2.0 to 2.8 (depending on the molecular weight and the test temperature. When the temperature is raised from 25°C to 150°C, the dielectric constant decreases (Fig. 38).

Figure 39 shows the dependence of the specific gravity of polydimethylsiloxanes on the degree of polymerization and on the temperature. The specific gravity of all polydimethylsiloxanes is less than 1, and decreases regularly with increasing temperature from 25°C to 150°C.

The dielectric constants and the densities approach a constant quantity as the number of silicon atoms in the polymer molecule increases.

Figure 40 gives the relation between the dielectric constant of polymethylsiloxane liquids and their viscosity, while their content of volatiles is shown in Fig. 41 (determined by heating at 200°C for 46 hours).

A definite relation exists between specific gravity and dielectric constant (Bibl. 63). With increasing number of silicon atoms in the polymer molecule, both these characteristics at first increase, and then approach a limit, after which
they remain almost unchanged with further increase in the number of silicon atoms in the molecule.

The temperature-dependence of the specific volume of polydimethylsiloxane liquids decreases regularly with increasing size of the molecule, both in cyclic and linear polymers. The decrease in specific volume is greater in the linear compounds than in the cyclical. In absolute value, the specific volume of a linear compound is greater than that of a cyclic compound containing the same number of silicon atoms in its molecule. With increasing size of the molecules, the difference between the specific volumes of cyclic and linear compounds lessens.

Figure 42 shows the temperature variation in the volume of polymethylsiloxane liquids of different viscosities. The viscosity of polydimethylsiloxanes depends on temperature: there is a linear relation between the logarithm of the viscosity and the reciprocal of the absolute temperature. This linear relation shows that the

![Graphs](image-url)
Polydimethylsiloxanes are "normal" liquids with a very low degree of association. In linear polydimethylsiloxanes the association is greater than it is in the cyclic compounds. This is confirmed by measurements of viscosities, molar and specific volumes, etc.

The temperature dependence of the viscosity of polymethylsiloxane liquids and of petroleum oils is shown in Fig.43.

Polydimethylsiloxane liquids are considerably less volatile, have higher flash points, and are more resistant to oxidation, than petroleum oils of the same viscosity. They freeze at lower temperatures.

Polymethylsiloxane liquids with the required characteristics are prepared by separating narrow cuts of product by fractional distillation, and selecting the fraction of the desired viscosity. On hydrolysis of dimethyldichlorosilane and trimethylchlorosilane, hexamethyldisiloxane and cyclic compounds, trimer, tetramer,
pentamer, etc., are always formed besides the linear polymers.

A convenient method of preparing liquid polymers with linear molecules is the rearrangement of polydimethylsiloxanes by the action of sulfuric acid in the presence of hexamethyldisiloxane. For this purpose, the product of hydrolysis of dimethyldichlorosiloxane in an acid medium, for instance octamethylcyclosiloxane, is mixed in proper proportions with hexamethyldisiloxane (calculated for the formation of a chain of the required average length), and about 70% by volume of conc. sulfuric acid is added to the mixture. The average chain length is determined very exactly by the proportions of the reagents (of the cyclic polymer and the hexamethyldisiloxane). The mixture is shaken at room temperature until equilibrium is established (when constant viscosity is attained). After equilibrium has been reached, 20% by volume of water is added, and the shaking is continued for several hours. An oil is formed during the hydrolysis of the sulfuric acid groups. The acid is removed, and the oil is neutralized and dried. Under the proper pressure, the volatile products can easily be distilled off from the equilibrium mixture. This makes the remaining polymers still more uniform. The properties of linear polymers with 2 to 11 silicon atoms in the molecule have
been studied, showing a linear relation between the logarithm of the vapor pressure and the reciprocal of the absolute temperature. The logarithm of the vapor pressure also has a linear relation to the number of silicon atoms in the polymer; and the vapor pressure of linear polymers is lower than that of cyclic polymers with the same number of silicon atoms. The latent heat of evaporation is in linear relation to the number of silicon atoms in the polymer. It is smaller in cyclic polymers than in the corresponding linear compounds, and this difference increases with the number of silicon atoms in the polymer.

The heat of evaporation of linear polydimethylsiloxanes is determined by the empirical formula:

\[
\Delta H_{\text{linear}} = 4.70 + 1.65x
\]

where \( x \) = number of silicon atoms in the chain.

The heat of evaporation of cyclical polymers is calculated by the formula:

\[
\Delta H_{\text{cyclic}} = 5.45 + 1.35x
\]

where \( x \) is the number of \( \text{R}_2\text{SiO} \) structural units.

At the same temperature, a linear polymer has a lower vapor pressure than the corresponding cyclic polymer.

It has been found that the logarithm of the absolute viscosity is a linear function of the logarithm of the number of units in the chain. The corresponding cyclic polymer always has a higher viscosity than the linear polymer, and its viscosity varies more rapidly with the temperature.

Two experiments were performed to determine the relation between the composition of an equilibrium mixture of polydimethylsiloxanes and the conditions of its preparation (in the absence of a solvent, and in its presence).

In the first experiment a mixture of 177 g of hexamethyldisiloxane and 323 g of
octamethylcyclotetrasiloxane was treated with 5 ml. of conc. sulfuric acid and shaken on a shaking machine for 21 days at room temperature (Bibl. 614). The equilibrium state was followed from the change in the viscosity of the solution. During the first 5 days, the viscosity increased from 1.01 to 2.5 centipoises, and thereafter remained constant. After 21 days the mixture was washed with water to remove the acid, dried over anhydrous sodium carbonate, and fractionated.

In the second experiment a mixture of 177 g of hexamethyldisiloxane, 323 g of octamethylcyclotetrasiloxane, and 8040 g of carbon tetrachloride was taken. To the mixture 16 g of antimony pentachloride was added, after which it was shaken 23 days on the shaking machine at 25°C. In 8 days the viscosity of the mixture increased from 0.901 to 0.932 centipoises, thereafter remaining constant. After termination of the experiment, the mixture was washed with water to remove the antimony pentachloride, the CCl₄ was distilled off, and the residue was fractionated in a column.

When the carbon tetrachloride was distilled off, some of the hexamethyldisiloxane in the mixture was also volatilized. Special experiments showed that 6.6% of the hexamethyldisiloxane was so distilled with the CCl₄.

The starting mixture contained (by weight) 35% of hexamethyldisiloxane and 64.6% of octamethylcyclotetrasiloxane. The percentage compositions of the mixture obtained after the action of sulfuric acid (Experiment 1) according to the above technique, and of antimony pentachloride (Experiment 2) in CCl₄ solution, were as follows.

<table>
<thead>
<tr>
<th>Linear polymers:</th>
<th>Experiment 1</th>
<th>Experiment 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>dimer</td>
<td>6.5</td>
<td>10.1</td>
</tr>
<tr>
<td>trimer</td>
<td>8.7</td>
<td>11.7</td>
</tr>
<tr>
<td>tetramer</td>
<td>9.7</td>
<td>10.5</td>
</tr>
<tr>
<td>pentamer</td>
<td>10.0</td>
<td>9.0</td>
</tr>
<tr>
<td>hexamer</td>
<td>8.3</td>
<td>6.5</td>
</tr>
<tr>
<td>heptamer</td>
<td>7.8</td>
<td>5.5</td>
</tr>
<tr>
<td>octamer</td>
<td>6.6</td>
<td>4.3</td>
</tr>
<tr>
<td>Cyclic polymers:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>tetramer</td>
<td>3.1</td>
<td>21.3</td>
</tr>
<tr>
<td>pentamer</td>
<td>0.8</td>
<td>7.2</td>
</tr>
</tbody>
</table>

Cyclic hexa-, hepta- and octamers were found in small quantities.
It is interesting to note that the data obtained by calculating the theoretical composition of the mixture, based on the Flory method, were in agreement with the observed values (with deviations not over 1.2% in either direction).

We now present a description of the method of calculating the composition of a mixture of polydimethylsiloxanes in an equilibrium system (Bibl. 61). Notation used:

- **M** - end groups \((\text{CH}_3)_3\text{SiO}\);
- **D** - unit of chain \((\text{CH}_3)_2\text{SiO}\);
- **x**, **y** - number of units in original molecules
- **z** - number by which the number of units in the molecules formed has varied;
- **r_y** - molar concentration of cyclic polymers containing **y** units in the molecule.

The reaction between the linear polydimethylsiloxanes, leading to equilibrium, may be described as follows:

\[
\text{MD}_{x-y}M + \text{MD}_{y-z}M = \text{DM}_{x+z-y}M + \text{MD}_{y-z}M
\]

The equilibrium constant of this reaction may be expressed in terms of the concentrations of the components of the mixture, and does not depend on the values of **x**, **y** and **z**.

\[
K = \frac{C_{x+z}C_{y-z}}{C_xC_y} = 1
\]

The experimental data are very close to the theoretical. Thus, the value of the equilibrium constants of linear polymers for 15 equilibria studied deviates, in the maximum case, only by 0.32. In spite of the applicability of the Flory method to an infinitely long chain, satisfactory correspondence between theoretical and experimental data is also observed in this case.

For the reaction of conversion of a linear polymer into a mixture of a cyclic and a linear polymer with shorter chains.
The equilibrium constant should depend on \( y \), that is, on the number of units in the ring. The equation of the equilibrium constant in this case will be of the following form:

\[
K_y = \frac{R_y C_x}{C_{x+y}}
\]  

(2)

Since no cyclical trimer was found in the process of establishing equilibrium or in the equilibrium system, it must be concluded that, for \( y \leq 4 \), the equilibrium constant \( K_y = 0 \).

For \( y = 4 \), 5, and 6, the equilibrium constant varies. On the basis of experimental data, the curve of the relation between \( K_y \) and the value of \( y \) was plotted.

\[
K_y = 11.0(0.40)^y \text{ for } y > 3
\]  

(3)

It should be noted that this equation holds only for the given system, and that in any other case the values of the coefficients will be different.

Equation (1) should correspond to the relation

\[
C = AP^x
\]

(4)

where \( A \) and \( P \) are constants for a given equilibrium system of polymethylsiloxanes.

If, now, we substitute the values of \( C \) and \( C_y \) in eq.(3), then we get:

\[
y < 4: \quad r_y = 0
\]

(5)

Cancelling out \( P^X \), we get

\[
R_y = 11(0.40)^y \text{ for } y > 4
\]

(6)
Since there are two \((\text{CH}_3\text{)}_3\text{Si}\) groups in each linear polydimethylsiloxane, the total molar concentration of these groups in the mixture of polymers in the equilibrium state will be equal to:

\[
M = \frac{2C_x}{x=2}
\]  

(7)

The total molar concentration of the \((\text{CH}_3\text{)}_2\text{SiO}\) groups will be made up of the sum of these groups in the linear and cyclic polymers:

\[
D = \sum_{x=2} C_x + \sum_{y=4} yry
\]  

(8)

Substituting the value of \(C_x\) for eq.(4) and of \(y\) from eq.(6), we obtain:

\[
\frac{1}{1 - P} = \frac{2AP^3}{1 - P} + \frac{A^4 \times (0.40P)^4 - 33.0(0.40P)^8}{1 - 0.40P^2}
\]  

(9)

Knowing the total concentration of the \(M\) and \(D\) units, \(A\) and \(P\) may now be calculated, after which, by substituting the values so found in eqs.(4) and (6), the concentration of any dimethylsiloxane polymer in an equilibrium system may be found.

Starting out from these equations, the degree of polymerization of the mixture of polymers in a given equilibrium system may also be calculated. If the degree of polymerization is defined as the ratio of the sum of the concentrations of all the elementary units \(M\) and \(D\) to the sum of the concentrations of all cyclic and linear polymers, then the following relation is obtained:

\[
\frac{1}{1 - P} = \frac{2AP^3}{1 - P} + \frac{A^4 \times (0.40P)^4 - 33.0(0.40P)^8}{1 - 0.40P^2}
\]
Substituting the corresponding values in this equation, we get:

\[
\frac{1}{\mu_n} = \frac{A(2P^2 - P^4)}{(1 - P)^4} + \frac{44(0.40P)^4 - 33(0.40P)^6}{(1 - 0.40P)^6}
\]

Experimental determination of the degree of condensation of the system coincided exactly with the theoretically calculated value. The fact that no cyclical trimer was found in investigating the equilibrium polydimethylsiloxane system points to the existence of great stresses in the six-membered ring constructed of silicon and oxygen atoms. The silicon-oxygen angle in polydimethylcyclosiloxanes is 160°15'. Thus, in the six-membered ring, whose angle is almost 109°28', there are great stresses.

High stresses may originate in the rings of cyclic hydrocarbons owing to the interference of substituent groups or hydrogen atoms. In the case of polysiloxane rings, the substituent groups are further apart and interact less with each other.

When a trifunctional monomer, methyltrichlorosilane (Bibl.65) is introduced into the process of cohydrolysis of dimethyldichlorosilane with trimethylchlorosilane, the siloxane groups obtained are more or less branched (depending on the relative number of trifunctional units introduced). In this case each branch is closed by a \((\text{CH}_3)_3\text{SiO}\) group, which preserves the chemical stability of the liquid.

The branched polymethylsiloxanes are also subject to rearrangement under the action of sulfuric acid. When this occurs, great changes in molecular size are observed, and under appropriate pressure large quantities of light fractions are distilled off. The viscosity-temperature coefficient of the polymer so obtained does not exceed 0.67 (for oils based on hydrocarbons, 0.8–0.9), and the freezing point sometimes goes as low as −89°C. The change of physical properties in this case may be explained mainly by the formation of cyclic macromolecules.

The slight change of viscosity of a polysiloxane oil with the temperature may be vividly illustrated by the following example: if a polymethylsiloxane oil and a
standard hydrocarbon oil have the same viscosity at 100°C, then, when both are cooled to -35°C, the viscosity of the former will increase 7 times, and that of the latter 1800 times. The slight temperature variation of the viscosity of polymethylsiloxane oils makes them particularly advantageous for use as working liquids in hydraulic systems. They do not react with the ordinary metals, maintain their color and do not oxidize at 200°C. They have satisfactory lubricating properties.

Polyethyldimethylsioxane Liquids

When a mixture of diethyldichlorosilane and triethylchlorosilane is hydrolyzed by water in an acid medium, as in the hydrolysis of the methylchlorosilanes, liquid polymers with a wide boiling range are obtained. The quantity of the high-boiling fractions depends on the conditions of hydrolysis, and increases with the ratio between the quantity of diethyldichlorosilane to that of triethylchlorosilane.

The liquids obtained by the hydrolysis of a mixture of diethyldiethoxysilane and triethylethoxysilane boil over a wide range of temperatures.

Table 92 (cf. p.759) give the principal physico-chemical properties of polyethyldimethylsioxane liquids.

The liquids prepared from the ethyl-substituted esters of orthosilicic acid have a higher viscosity than liquids boiling at the same temperature but prepared from the ethylchlorosilanes. The existence of an ester value, due to the presence of ethoxy groups, is characteristic for them.

The presence of ethoxy groups sharply affects the viscosity of the polymer. This will be clearly seen from Fig.44, showing the viscosity-temperature dependence of liquids with boiling points close together but prepared: some from ethylchlorosilanes, others from ethyl-substituted esters of orthosilicic acid.

Studies of the dielectric properties of the liquids prepared from a mixture of diethyldimethylsilanol and triethyldimethylsilanol have shown them to possess high volume resistivity, which, however, depends on the test temperature and the molecular weight of the liquid (cf.Fig.45).
Table 92

Properties of Polyethyilsiloxane Liquids

<table>
<thead>
<tr>
<th>Boiling Point, °C</th>
<th>Specific Gravity</th>
<th>Viscosity Centistokes</th>
<th>Refractive Index, nD</th>
<th>Acid Value</th>
<th>Freezing Point, °C</th>
<th>Flash Point, °C</th>
<th>Fire Point, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 - 80 (6 mm)</td>
<td>0.8127</td>
<td>1.020</td>
<td>1.4471</td>
<td>2.95</td>
<td>Under -110</td>
<td>40</td>
<td>56</td>
</tr>
<tr>
<td>60 - 100 (6 mm)</td>
<td>0.8661</td>
<td>2.00</td>
<td>1.4360</td>
<td>1.87</td>
<td>Under -110</td>
<td>78</td>
<td>100</td>
</tr>
<tr>
<td>100 - 150 (6 mm)</td>
<td>0.9045</td>
<td>3.3</td>
<td>1.4375</td>
<td>1.59</td>
<td>Under -110</td>
<td>100</td>
<td>110</td>
</tr>
<tr>
<td>150 - 237 (8 mm)</td>
<td>0.9835</td>
<td>10.2</td>
<td>1.4405</td>
<td>2.05</td>
<td>Under -110</td>
<td>110</td>
<td>160</td>
</tr>
<tr>
<td>Over 237 (8 mm)</td>
<td>—</td>
<td>—</td>
<td>1.4491</td>
<td>4.84</td>
<td>Under -110</td>
<td>208</td>
<td>255</td>
</tr>
</tbody>
</table>

Liquids prepared from a mixture of diethyldichlorosilane and triethyltrichlorosilane

<table>
<thead>
<tr>
<th>Boiling Point, °C</th>
<th>Specific Gravity</th>
<th>Viscosity Centistokes</th>
<th>Refractive Index, nD</th>
<th>Acid Value</th>
<th>Freezing Point, °C</th>
<th>Flash Point, °C</th>
<th>Fire Point, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>150 - 200 (6 mm)</td>
<td>—</td>
<td>9.50</td>
<td>—</td>
<td>0.85</td>
<td>-109</td>
<td>125</td>
<td>145</td>
</tr>
<tr>
<td>200 - 282 (8 mm)</td>
<td>—</td>
<td>87.43</td>
<td>—</td>
<td>1.57</td>
<td>-94</td>
<td>153</td>
<td>214</td>
</tr>
</tbody>
</table>

An advantage of these liquids is the fact that in them this dependence is considerably less pronounced than in purified transformer oils, owing to the fact that their viscosity-temperature coefficients are lower than in mineral oils.

Figure 46 shows the temperature-dependence of the tangent of the dielectric loss angle at 50 cycles. The dielectric losses in the high temperature region very strongly depend on the purity of the liquid.

Figure 47 shows the temperature-dependence of the tangent of the dielectric loss angle at various frequencies.

At temperatures above 0°C, the tangent of the dielectric loss angle and the dielectric constant maintain constant values for each of these frequencies. At low
temperatures, the tangent of dielectric loss angle begins to increase, and approaches a maximum, which indicates the existence of orientation losses. The existence of orientation losses compels us to assume that their appearance must be due to contaminations, either owing to polar OH or OR groups remaining in the composition of the molecule, or owing to the Si-O bond. At higher temperatures, at all frequencies, only displacement losses, not depending on the temperature, are observed. No losses of conductivity up to 100°C are manifested (Bibl.66).

Figure 4.4 shows the relation between the viscosity of polyorganosiloxane liq-

Fig. 4.4 - Temperature-dependence of Relative Viscosity of Polydiethylsiloxane Oils with Different Boiling Points:
1 - oil from ethylchlorosilanes (b.p. 100-200°C at 1 mm); 2 - oil from ethylchlorosilanes (b.p. 150-200°C at 1 mm)
3 - oil from ethyl-substituted esters (b.p. 100-200°C at 1 mm); 4 - oil from ethyl-substituted esters (b.p. 150-200°C at 1 mm)

Fig. 4.5 - Temperature-dependence of the Volume Resistivity of Polyethylsiloxane Liquids:
1 - liquid of b.p. 150-200°C (8 mm); 2 - liquid of b.p. 200-215°C (8 mm)

a) Temperature, °C; b) Volume Resistivity, ohms/cm
uids and the average molecular weight.

As will be seen from the following data, liquid polymers containing a large number of ethoxy groups have considerable dipole moments:

![Diagram](image-url)

**Fig. 46 - Dependence of the Tangent of the Dielectric Loss Angle of a Polydiethylsiloxane Liquid on: Purity and Test Temperature**

1 - Liquid before purification; 2 - Liquid purified by adsorbents

- a) Temperature, °C; b) Tangent of dielectric loss angle

<table>
<thead>
<tr>
<th>Chemical Formula</th>
<th>Dipole Moment $10^{18}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(C_2H_5)_8O_3Si_4(OC_2H_5)_2$</td>
<td>2.60</td>
</tr>
<tr>
<td>$(C_2H_5)_{10}O_6Si_5(OC_2H_5)_2$</td>
<td>2.98</td>
</tr>
<tr>
<td>$(C_2H_5)_{16}O_7Si_6(OC_2H_5)_8$</td>
<td>3.28</td>
</tr>
<tr>
<td>$(C_2H_5)_{12}O_5Si_7(OC_2H_5)_7$</td>
<td>3.50</td>
</tr>
<tr>
<td>$(C_2H_5)_{18}O_6Si_7(OC_2H_5)_9$</td>
<td>3.56</td>
</tr>
</tbody>
</table>
Fig. 47 - Temperature dependence and Frequency dependence of Tangent of Dielectric Loss Angle of Polydiethylsiloxane Liquid (Fraction of b.p. 150-200°C, at 8 mm):

1 - 50 kilocycles; 2 - 100 kilocycles; 3 - 500 kilocycles; 4 - 1000 kilocycles

a) Temperature, °C; b) Tangent of dielectric loss angle

Fig. 48 - Relation Between Viscosity of Various Polyalkylsiloxane Liquids and their Average Molecular Weight:

1 - \([\text{Si} \left(CH_3\right)_4]_2\); 2 - \([\text{Si} \left(CH_3\right)_2\left(CH\right)_2\]_2\); 3 - \([\text{Si} \left(CH\right)_3\left(CH\right)_2\]_2\); 4 - \([\text{Si} \left(CH\right)_3\left(CH\right)_2\]_2\)

a) Average molecular weight; b) Viscosity at 25°C, centistokes

Polyalkylaryl Siloxane Liquids

Polyalkylaryl siloxane liquids may be prepared by the hydrolysis of phenylethylidichlorosilane, a phenylethylidialkoxy silane, or by co-hydrolysis of the corresponding dialkyl- and diaryldichloro- or dialkoxy silanes.

The hydrolysis of phenylethylidichlorosilane is conducted in two stages. In the first stage it is slowly poured into a mixture of ethanol and water; the polymer so obtained is an oil of viscosity not exceeding 60 centistokes.

In the second stage, this oil is treated a few hours at 130-140°C with solid caustic soda (the molar ratio of the caustic soda to the silicon is 1:25).

After the treatment, the product is washed and dried. The viscosity of the product is now 5000 centistokes.

Similar products are prepared by the hydrolysis of phenylmethyldichlorosilane;
before treatment with NaOH its viscosity is 332 centistokes, after treatment, 1100 centistokes.

Liquid copolymers have also been prepared by this method from the following products: phenylmethyldiethoxysilane + SiCl; phenylmethyldiethoxysilane + dimethyldiethoxysilane; phenylmethyldichlorosilane + phenylmethyldichlorosilane; phenylethylchlorosilane + tetraethoxysilane; ethyltrichlorosilane + diethylchlorosilane and dimethyldiethoxysilane.

A copolymer consisting of 4.0 mols of polyphenylethylcyclosiloxane $(C_6H_5C_2H_5SiO)n$, 49 mols of polydimethylcyclosiloxane $[(CH_3)2SiO]n$, and 11 mols of trimethylsilanol $(CH_3)_3SiOH$, is recommended for use as a lubricant.

The viscosity of polyorganosiloxane liquids is considerably less dependent on the rotary speed than that of organic liquids.

Figure 49 shows the relation between the viscosity of lubricants of organic and polyorganosiloxane liquids and the rotary speed of a frictional connection.

Polyorganosiloxane oils have very valuable properties. They are inert, remain unchanged in the presence of oxygen and of the metals and plastics used in technology. They do not change color in the presence of atmospheric oxygen at temperatures up to 250°C. In the absence of atmospheric oxygen, for instance, in a closed or
evacuated space the oil does not change its color even at considerably higher temperatures. The use of inhibitors increases the resistance of the oils to oxidation by atmospheric oxygen. The polyorganosiloxane oils, when heated up to 150°C, show no effect on copper, bronze, brass, aluminum, magnesium, iron, steel, tin, lead, cadmium or chromium. In turn, these metals do not act on the oils. The oils are relatively inactive with respect to weak solutions of acids and alkalies, but they do react with concentrated alkalies and acids. Owing to the combination of these properties, the polyorganosiloxane oils find widespread application as hydraulic fluids, shock-absorber fluids, oils for vacuum pumps, as well as lubricating oils; and greases, etc., are also manufactured from them (Bibl.66).

Polyorganosiloxane Resins

The composition and structure of the molecules from which organosilicon resins are prepared predetermine the characteristic features of their properties. Thus the heat-resisting qualities of organosilicon resins depend on the size and nature of the organic radical (Bibl.67). For example, polymers containing aromatic radicals have greater thermal stability than polymers containing aliphatic radicals. The ratio between the number of organic radicals in a resin to the number of silicon atoms, the degree of polycondensation, and the structure of the polymer, all have a great influence on the elasticity of the resin. An increase in the number of radicals in the molecules of the starting organosilicon compounds (up to the ratio R/Si-2) favors the production of resins having good elasticity.

The degree of condensation of the product and the structure of the polymer obtained are of the greatest importance. The elasticity of a linear polymer increases with its average molecular weight. The elasticity of linear polymers is higher than that of space polymers, but if a linear polymer has a very small number of side bonds to a large number of units in the chain, then the elasticity of the resin will be sharply increased.

In the initial stage of condensation, resins are soluble in organic solvents.
They are readily soluble in alcohols, in benzene, toluene, ethyl acetate, amyl acetate, dichloroethane, and acetone, and in mixtures of these solvents. As the degree of condensation of the products increases, their solubility in the alcohols diminishes, but their solubility in aromatic hydrocarbons and in mixtures of such hydrocarbons with higher alcohols remains unaffected and is even somewhat improved.

The solubility of resins of the same degree of condensation increases with the size of the organic radical. The degree of condensation and the polymeric structure exert a great influence on the solubility of resins. As a rule, the solubility of resins decreases with increasing degree of condensation. The solubility falls with particular sharpness on the formation of polymers with a three-dimensional structure.

The oxidation of the higher polyalkylsiloxanes is considerably more rapid than that of the lower ones. The rate of cleavage of the alkyl groups from the siloxane chain by means of oxidation may be best measured by the time taken by the polymer to crumble and disintegrate at a specified temperature. Polymethylsiloxane has a high heat resistance at 200°C, while polyamylsiloxane crumbles and disintegrates relatively fast at this temperature. The benzyl radical, like the butyl and amyl radicals, is cleaved from the silicon more readily than the methyl radical during oxidation. The phenyl radical is very firmly bound to the silicon atom. Resins with molecules containing the phenyl radical possess high thermal stability. They are oxidized with considerably greater difficulty, and require more severe conditions to detach the phenyl radical by oxidation.

The attachment of a second phenyl radical to a single silicon atom considerably reduces the susceptibility of polydiphenylsiloxanes to the action of solvents. Polyphenylsiloxane resins are more brittle than polymethyl and polyethyisyloxane resins. The polyphenylmethylsiloxanes and polyphenylethylsiloxanes have the highest heat-resisting power, and at the same time also have the highest elasticity. The products of copolymerization of phenylsilanetriol and dimethylsilanediol or diethylsilanediol have a higher elasticity than the products of cocondensation of phenylsilanetriol...
with diphenylsilanediol.

The polyorganosiloxane resins have a low sensitivity to the action of water; their water resistance increases with the size of the organic radical entering the composition of the resin molecule.

**Polymethylsiloxane Resins**

The hydrolysis of a mixture of methyltrichlorosilane and dimethyldichlorosilane by water leads to the formation of hydroxyl-containing products, which on heating are converted into resins.

To obtain thermoreactive resins, the ratio between the number of methyl radicals and the number of silicon atoms in the starting mixture must be less than 2. Under this condition the polymers will have a network molecular structure. By varying the ratio between the methyltrichlorosilane and the dimethyldichlorosilane taken for the hydrolysis, the number of cross-linkages between the molecular chains may be varied. This may be accomplished as well by oxidation of the condensation products by air or peroxides (Bibl.68). In particular, polymethylsiloxane resins containing three-dimensional molecules may be produced by the hydrolysis of dimethyldichlorosilane, followed by oxidation with air in the presence of a catalyst, and in the process of polycondensation the composition of the resin may be brought to the desired R/Si ratio.

Polymers (resins) with a network structure may also be prepared by hydrolysis of a mixture of dimethyldichlorosilane and methyltrichlorosilane or SiCl$_4$, followed by polycondensation of the hydrolysis products. In this case, the desired R/Si ratio in the resin may be attained by selection of the proper quantities of the components of the mixture, without using oxidation, since the cross-linked structure is obtained on account of the structural units formed by methyltrichlorosilane, and not by oxidation of part of the methyl groups, as in the first method.

The method of oxidation has the advantage over the method of cohydrolysis of not requiring the use of solvents during the hydrolysis. The second method requires
the hydrolysis to be conducted in the presence of solvents capable of dissolving both the products of hydrolysis and the resin produced as a result of hydrolysis and condensation. In the absence of solvents, and with a small amount of water, a high concentration of HCl will be obtained, which leads to the coagulation of the resin.

Preparation of polymethylsiloxane resins (Bibl.69). 1. A mixture of 181 parts by weight of butanol and 139 parts by weight of methylchlorosilanes is boiled 1.5 hours under a reflux condenser, until the evolution of HCl has ceased. After the mixture has cooled, 325 parts of water are added to it, and it is heated 3 hours. The oil so obtained is separated from the water layer. If the methylchlorosilane taken for the hydrolysis contains very little trimethylchlorosilane (chlorine content 63.6%), then the resin formed from the oil so separated hardens in 3 hours at 190°C, forming a flexible film that is heat-resistant at 200°C.

2. A solution of 100 g of methylchlorosilanes in 70 g of toluene is poured during a period of 5 min., with stirring, into a mixture of 200 g of ice, 70 g of water, and 70 g of butanol. The stirring is continued for 10 min. more. The temperature rises during the hydrolysis to 50°C. The hydrolysis product is then condensed or used in the uncondensed form. The cohydrolysis of 5.5 mols of a dialkyldichlorosilane with not more than 1.5 mols of SiCl₂ may be conducted by the same method.

3. A mixture of 90 parts of dimethyldiethoxysilane, 10 parts of methyltriethoxysilane, and 100 parts of a mixture of ethanol and HCl (in ratio 1:1), is heated ¼ hours in a flask with a reflux condenser. Then 10 parts of trimethylethoxysiloxane is dropwise added, and the heating is continued for another hour. The product is washed and the low-molecular substances are removed from it by distillation up to 230°C. The viscosity of the product so obtained is 45.5 centistokes at 25°C. Gelation of the resin takes place on heating 256 hours at 200°C. If the trimethylethoxysilane is added to the mixture before hydrolysis, then the end-product will have a viscosity of 21.9 centistokes, and gelation will occur on heating 63 hours at 200°C.

F-TS-9191/V
Polymethylsiloxane products prepared from methylchlorosilanes (CH₃/Si ratio 1.2; 1.3; 1.4 and 1.5) immediately after hydrolysis are colorless liquids of sp.gr. from 1.20 to 1.06. The time required for them to harden at 100°C ranges from 2 to 24 hours.

The refractive index of the resin is in linear relation with its content of methyl groups.

Resins with a CH₃/Si ratio less than 1.2 are tacky and sirupy liquids, which harden at room temperature, or on moderate heating, into a solid brittle glassy mass. At a CH₃/Si ratio over 1.7 (in the products to be hydrolyzed), oily products are obtained, which are converted into soft gels after heating a few days or weeks at 200°C (Bibl.70).

All polymethylsiloxane resins have a high thermal stability and good resistance to oxidation. Specimens of polymerized resins, heated to 550°C in vacuo or to 500°C in a stream of hydrogen, are not disintegrated and do not fuse for a long time. Heating the resins in air at 200°C causes no appreciable disintegration, while at 300°C it leads to slow oxidation.

On the thermal decomposition of polymethylsiloxanes no carbonaceous residues are formed (that is, there is no charring), which encourages their use for electrical insulation under conditions where a corona discharge may occur, or in high tension fields.

Polymethylsiloxane resins have the following dielectric properties:

Dielectric constant

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>at 26°C</td>
<td>3.7</td>
</tr>
<tr>
<td>at 56°C</td>
<td>3.6</td>
</tr>
</tbody>
</table>

Tangent of dielectric loss angle at 60 cycle frequency

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>at 26°C</td>
<td>0.008</td>
</tr>
<tr>
<td>at 56°C</td>
<td>0.0045</td>
</tr>
</tbody>
</table>
Polyethylsiloxane Resins

The polyethylsiloxane resins possess higher solubility, less hardness, and less tendency to polymerization, than the polymethylsiloxane resins. To obtain hard, infusible and insoluble polyethylsiloxane resins, the polymers must contain a smaller number of ethyl radicals per silicon atom than there are methyl groups in the polymethylsiloxane resins. The optimum $C_2H_5/Si$ ratio in the polyethylsiloxane resins lies in the range from 0.5 to 1.5.

If this ratio is lower than 0.5, then the resin polymerizes rapidly, turning into a glassy product that easily disintegrates at high temperatures. Such resins have a highly branched, cross-linked structure, and become insoluble already at the early stages of condensation, which makes their utilization difficult. The excessive shrinkage, owing to the relatively large quantities of water liberated during the course of the condensation, causes internal stresses making the mass of the resin brittle and weak, and leads to its disintegration.

If the $C_2H_5/Si$ ratio in the polymer is over 0.5, then such a polymer will have a resinous appearance and will have little resemblance to brittle glass. With increasing value of this ratio, the softness and elasticity of the polymer increase.

Polymers with a $C_2H_5/Si$ ratio of 1 to 1.5 are plastic. They are more difficult to convert into the hard state, requiring the use of catalysts. Polymers with two ethyl radicals attached to a single silicon atom are typical elastomers.

The resins prepared from ethyl-substituted esters of orthosilicic acid and ethylchlorosilanes have been studied in greater detail.

The relationship between the viscosity and molecular weight of the polydiethylsiloxanes has been established. For this purpose, polydiethylsiloxanes were subjected to repeated fractionation under high vacuum or to repeated fractional dissolution and precipitation, resulting in fractions consisting of molecules of approximately the same degree of condensation.

The constant $K_m$ entering into the equation of viscosity has been determined.
This constant, for the Si-O unit of the chain (Bibl.75) in alcohol is $1.45 \times 10^{-4}$; in benzene it is $1.43 \times 10^{-4}$.

Using this constant, the variation of the average values of the molecular weight of polyethyilsiloxanes was studied, both in the process of the reaction of formation of low molecular products and in the process of formation of high molecular products.

The viscosimetric determinations of the molecular weight of resins prepared from diethyldioethoxysilane, after the action of 1, 1.5, 2, and 5 moles of water, show that the average molecular weight as a rule increases with the quantity of water taken in the reaction. Figure 50 shows the relationship between the average molecular weight of polycondensation products obtained from diethyldioethoxysiloxane and the quantity of water taken for the hydrolysis.

It will be clear from Fig. 50 that the average molecular weight of the polymer after 10 hours of condensation is 3700. The conduct of the reaction for a longer period leads to the formation of higher molecular products with an average molecular weight of about 6000 (Fig. 51).

The increase of the average molecular weight is slowed as the condensation deepens. This will be seen from the slope of the curve. The slowing in the rise of the average molecular weight on prolonged condensation is due to the decrease in the number of reacting particles, and to the decrease in the mobility in the molecules owing to the increased viscosity of the polymer.

The relatively low average molecular weight of the above resins is explained by the fact that they were prepared under conditions when, during the process of
the reaction, the alcohols liberated on the hydrolysis of the ethoxy end groups were
not removed, but remained in the reaction medium. The action of aqueous alcohol on
diethylidioethoxysilane, with simultaneous removal of the alcohol formed during con-
densation, leads to the formation of products with considerably higher average mo-
lecular weight.

On fractionation of polydiethylsiloxane resin by dissolving it in various sol-
vents, followed by fractional precipitation, nonuniform fractions were obtained.

Fig. 50 - Relation of the Molecular
Weight of the Hydrolyzates of Diethyl-
dioethoxysilane to Time of Condensa-
tion, and to Quantity of Water Taken
for the Hydrolysis of 1 mol of di-
edethylidioethoxysilane:
1 - 1 mol of water; 2 - 1.5 mols of
water; 3 - 2 mols of water; 4 - mols
of water
a) Time of condensation, hours;
b) Molecular weight

Fig. 51 - Relation between Molecular
Weight and Time of Condensation
a) Time of condensation, hours;
b) Molecular weight

The difference in the solubility
and other physical properties between
the individual members of the homolo-
gous polymer series of polyethylsilox-
anes is exceptionally small, and it de-
creases with lengthening molecular
chain. This circumstance makes it prac-
tically impossible to separate completely uniform individual polydiethylsiloxane
compounds. Thus, even after 28 precipitations of a resin (resin with average molec-
ular weight of 2628 and average degree of polycondensation 25), it was not possible
to isolate an individual product. The separation of the resin into fractions was performed by its fractional precipitation by petroleum ether from a benzene solution.

Table 93 gives the results of the study of the fractions of a resinous product of average molecular weight 2628.

Table 93

Characteristics of Fractions Obtained from a Resin of Molecular Weight 2628

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Yield g</th>
<th>% Wt. of principal polymer fraction</th>
<th>Average Molecular Weight (determined cryoscopically in benzene)</th>
<th>Molecular Weight (determined from viscosity)</th>
<th>Average degree of polymerization</th>
<th>Found</th>
<th>Calculated</th>
<th>Molecular Weight (determined by chemical method)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original Resin</td>
<td>28</td>
<td>0.120</td>
<td>6282</td>
<td>6115</td>
<td>61</td>
<td>1.58</td>
<td>1.42</td>
<td>5800</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>0.192</td>
<td>---</td>
<td>10105</td>
<td>99</td>
<td>0.92</td>
<td>0.89</td>
<td>9800</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>0.170</td>
<td>---</td>
<td>8947</td>
<td>87</td>
<td>0.94</td>
<td>1.101</td>
<td>9574</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>0.151</td>
<td>---</td>
<td>7947</td>
<td>77</td>
<td>0.01</td>
<td>1.13</td>
<td>8400</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>0.112</td>
<td>---</td>
<td>5894</td>
<td>57</td>
<td>1.42</td>
<td>1.53</td>
<td>---</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>0.092</td>
<td>---</td>
<td>4842</td>
<td>47</td>
<td>1.98</td>
<td>1.86</td>
<td>4600</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0.084</td>
<td>---</td>
<td>4431</td>
<td>43</td>
<td>2.14</td>
<td>2.03</td>
<td>4296</td>
</tr>
</tbody>
</table>

Table 94 gives the results of a study of the fractions of a resinous product of average molecular weight 6282.

Table 94

Characteristics of Fractions Obtained from a Resin of Molecular Weight 6282

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Yield g</th>
<th>% Wt. of principal polymer fraction</th>
<th>Average Molecular Weight (determined cryoscopically in benzene)</th>
<th>Molecular Weight (determined from viscosity)</th>
<th>Average degree of polymerization</th>
<th>Found</th>
<th>Calculated</th>
<th>Molecular Weight (determined by chemical method)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original Resin</td>
<td>28</td>
<td>0.120</td>
<td>6282</td>
<td>6115</td>
<td>61</td>
<td>1.58</td>
<td>1.42</td>
<td>5800</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>0.192</td>
<td>---</td>
<td>10105</td>
<td>99</td>
<td>0.92</td>
<td>0.89</td>
<td>9800</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>0.170</td>
<td>---</td>
<td>8947</td>
<td>87</td>
<td>0.94</td>
<td>1.101</td>
<td>9574</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>0.151</td>
<td>---</td>
<td>7947</td>
<td>77</td>
<td>0.01</td>
<td>1.13</td>
<td>8400</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>0.112</td>
<td>---</td>
<td>5894</td>
<td>57</td>
<td>1.42</td>
<td>1.53</td>
<td>---</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>0.092</td>
<td>---</td>
<td>4842</td>
<td>47</td>
<td>1.98</td>
<td>1.86</td>
<td>4600</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0.084</td>
<td>---</td>
<td>4431</td>
<td>43</td>
<td>2.14</td>
<td>2.03</td>
<td>4296</td>
</tr>
</tbody>
</table>

It may be concluded from these experimental data that the resins prepared from diethyldiethoxysilane consist mainly of a mixture of molecules of the following type:

F-TS-9191/V
Consequently, when hydrolysis is conducted in a neutral medium, using an amount of water close to the theoretical, practically no formation of cyclic polymers is observed.

In studying the process of formation of resins from diethyldichlorosilane and diethyldisilaneol, the viscosimetric method was also used to determine the average molecular weight of the polymer. The constant $K = 1.45 \times 10^{-4}$, determined previously for the products of hydrolysis and condensation of diethyldiethoxysilane, was used to calculate the molecular weight of the polymer formed. The resins examined were prepared from diethyldichlorosilane by treating it with 3 mols of water at $85^\circ$C, and from diethyldisilaneol by treating it 3 hours at $85^\circ$C.

The molecular weight was determined both for the end product and during the process of polycondensation of the resin.

After 10 hours of condensation, the molecular weight of a resin from diethylsilaneol reaches $5400$, and that of a resin from diethyldichlorosilane $4650$; further condensation leads to the formation of product difficultly soluble in the usual solvents.

By fractional dissolution of the resin prepared from diethyldisilaneol, two fractions could be separated (cf. Table 95).

<table>
<thead>
<tr>
<th>Table 95</th>
</tr>
</thead>
</table>

**Characteristics of Fractions of Resins Prepared from Diethyldisilaneol**

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Yield</th>
<th>$g$</th>
<th>$\eta$ of principal ether solution</th>
<th>Average Mol. Wt. determined from viscosity</th>
<th>Mol. Wt. (determined by chemical method)</th>
<th>Degree of condensation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original resin</td>
<td>24.2</td>
<td>0.157</td>
<td>5401</td>
<td>5387</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td>Fraction soluble in alcohol</td>
<td>12.4</td>
<td>0.132</td>
<td>4551</td>
<td>4341</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>Fraction soluble in benzene</td>
<td>8.1</td>
<td>0.1</td>
<td>6483</td>
<td>6278</td>
<td>60–71</td>
<td></td>
</tr>
</tbody>
</table>
Here, as in the preparation of the products of hydrolysis and condensation of diethyldiethoxysilane, the values of the molecular weight determined viscosimetrically and chemically are in good agreement. This indicates the linear structure of the molecules entering into a composition of the resin.

Resins from Ethyltriethoxysilane

In studying the structure and molecular weight of the resins obtained from ethyltriethoxysilane, the viscosimetric and chemical methods were also used, but, as was to be expected, the viscosimetric method gave less satisfactory results. This is probably to be explained by the fact that the hydrolysis of ethyltriethoxysilane leads to the formation of both branched and network molecules.

The determination of $K_M$ for the product of hydrolysis and condensation of ethyltriethoxysilane was performed on samples prepared by the hydrolysis of ethyltriethoxysilane by small amounts of water. The fractions were separated by distillation in high vacuum (Bibl.71). The small amounts of water were taken with the object of preventing the formation of branched molecules.

The elementary unit of the polymer chain formed, $-\text{Si}-\text{O}-$, has the molecular weight of 118.

For the products of hydrolysis and condensation of ethyltriethoxysilane in benzene, $K_M = 1.75 \times 10^{-4}$, and in alcohol $K_M = 1.57 \times 10^{-4}$.
A viscosimetric study of the average molecular weight of the products obtained on treatment of one gram-molecule of ethyltriethoxysilane with 1, 1.5, 2, and 3 mols of water, shows that the molecular weight increases with the amount of water taken in the reaction (Fig.52). The increase of the average molecular weight in unit time decreases as the process of condensation deepens. It should be noted that, with increasing quantity of water taken for the hydrolysis of ethyltriethoxysilane, the value of the average molecular weight of the condensation product, determined viscosimetrically, is somewhat lower than the average molecular weight of the resins prepared from diethylidisthosilxilane under the same conditions, while the rate of hydrolysis for ethyltriethoxysilanes, as had been shown previously, is considerably higher. This discrepancy is explained by the formation of branched molecules during the hydrolysis and condensation of ethyltriethoxysilane.

Table 96 gives the characteristics of the fractions prepared from such resins.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Yield %</th>
<th>Viscosity of resin in molar solution</th>
<th>Average mol. wt.</th>
<th>Mol. wt. determined from viscosity</th>
<th>Average degree of condensation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original resin</td>
<td>15</td>
<td>0.098</td>
<td>2128</td>
<td>2080</td>
<td>17-18</td>
</tr>
<tr>
<td>Fraction soluble in p. ether</td>
<td>2</td>
<td>0.084</td>
<td>1935</td>
<td>1783</td>
<td>16</td>
</tr>
<tr>
<td>Fraction soluble in benzene</td>
<td>48</td>
<td>0.110</td>
<td>2671</td>
<td>2035</td>
<td>22</td>
</tr>
<tr>
<td>Fraction sol. in ethanol</td>
<td>6.5</td>
<td>0.152</td>
<td>3812</td>
<td>3127</td>
<td>32</td>
</tr>
</tbody>
</table>

The initial products of hydrolysis and condensation of ethyltriethoxysilane are readily soluble in alcohol, benzene, alcohol-benzene mixtures, and toluene, but their solubility decreases with increasing degree of condensation of the products. On heating, they easily undergo further condensation, owing to the free hydroxyl groups. They undergo further condensation with particular ease when the heating takes place with access of air and moisture.

F-TS-9191/V 775
A number of substances may be used as catalysts of the process of hardening the resins. Such compounds include esters of boric acid, substituted orthoborates, antimony halides, metallic oxides, phosphorus halides and oxyhalides, sulfuric acid, boron halides, amines, activated aluminum, and activated silica gel. The amount of catalyst may range from 0.1 to 50% of the weight of the resins. When dimethylsilanediol is mixed with half the volume of ethyl borate and the mixture is heated to 190°C, a hard polymer is formed in 10 minutes, while without ethylborate, a few hours are necessary for the resin to harden. Liquid polymethylsiloxane, mixed with 20% by volume of ethyl borate, hardens on heating to 170°C for 30 minutes, while without ethyl borate this product is hardened under similar conditions only in a period of several days.

The use of the esters of boric acid as catalysts in preparing resins for electrotechnical articles is recommended. The use of alkyl borates is recommended as catalysts for the polymerization of alkylsilanols, and that of aryl borates for arylsilanols.

The influence of the catalyst on the rate of hardening of polymethylsiloxane will be seen from the following data.

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Time of Hardening</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without Catalysts</td>
<td>175</td>
</tr>
<tr>
<td>Antimony Pentachloride</td>
<td>15-20</td>
</tr>
<tr>
<td>Sulfuric Acid</td>
<td>15-20</td>
</tr>
<tr>
<td>Diethylamine</td>
<td>120</td>
</tr>
</tbody>
</table>

**Polyorganosiloxane Resins Containing Higher Organic Radicals**

The hydrolyzates of propylchlorosilanes, butylchlorosilanes, amylchlorosilanes, and hexylchlorosilanes, or of propyl, butyl, amyl, and hexyl-substituted esters of orthosilicic acid in the initial stage, are colorless or yellow viscous liquids. These liquids on heating form resins capable of conversion into infusible products.
The ability of these resins to pass into the infusible state depends on the reaction condition and on the R/Si ratio. With decreasing ratio between the number of radicals and the number of silicon atoms, the rate of hardening of the resins increases. The size of the organic radical has a substantial influence of the properties of the resins.

Polyalkylsiloxanes of the type \((RSiO\,\frac{1}{2})_n\), which are formed by hydrolysis of alkyltrichlorosilanes or mono-substituted esters of orthosilicic acids, are infusible glassy polymers. Among them, the polypropylsiloxanes are insoluble. The polyamylsiloxane resins will be soluble in ether and benzene, if the hydrolysis was run with insufficient water, and the hydrolyzates will contain linear polymers of the type \([RSi(OR)]_n\). On complete hydrolysis, stable polymers suitable for use as lacquers are formed.

The heat-resisting properties of organosilicon resins are considerably better than those of organic resins, and depend on the size of the organic radical. With the growth of this radical, the heat resistance diminishes. With one and the same radical, the heat resistance of the resin increases, according to Martens (Bibl.75) with the Si/\(R\) ratio.

**Polyaryl siloxane Resins**

On the hydrolysis of diphenyl dichlorosilane, in contrast to the hydrolysis of dimethyl- or diethyldichlorosilane, crystalline products are easily formed. The hydrolysis of diphenyl dichlorosilane in cold water in the presence of a solvent leads to the formation of diphenylsilanediol, which may be recrystallized and prepared in the pure form with a melting point of \(148^\circ\)C. If the crystals are dissolved in ether and heated with a small amount of concentrated HCl, then hexaphenylcyclotrisiloxane, \([(C_6H_5)_2SiO]_3\), is formed in high yield.

If the diphenylsilanediol is dissolved in boiling alcohol and a few drops of aqueous alkali are added to the solution so obtained, then, after cooling, crystals of octaphenylcyclotetrasiloxane are thrown down, which are easily separated from
the liquid. Evidently in the presence of powerful bases the tetramer is formed almost exclusively during the condensation of diphenylsilineol, while strong acids condense this monomer only to the timer. If diphenyl dichlorosilane is hydrolyzed incompletely, for instance under the action of only a quarter of the amount of water necessary for complete hydrolysis, then a number of dichloropolydiphenylsiloxanes are formed; among them, dichlorotetraphenylsiloxane and dichlorohexaphenyltrisiloxane have been isolated in the form of crystalline substances. These substances, being soluble in a mixture of alcohol and the hydrocarbon, are hydrolyzed very slowly, and form the corresponding dihydroxypolydiphenylsiloxanes under the action of cold water. As a result of the cohydrolysis of phenyl dichlorosilane with diphenyl dichlorosilane in an acid medium, oily liquids, or liquids containing a certain quantity of crystals, are formed. An elevated temperature during the hydrolysis and a strongly acid medium favor the formation of oils with a high content of crystalline substances (cyclic phenylhydroxysiloxanes).

Oils not containing crystalline products or containing only a small amount of them, are easily converted into resins on heating. Oils containing a large quantity of crystals form waxy products on heating, possessing the sharp transition from the solid to the liquid state, on melting, which is characteristic for waxes. Thus, from phenyltrichlorosilane and diphenyl dichlorosilane, according to the conditions of the cohydrolysis and condensation reaction, either resins or waxy substances can be obtained.

As stated above, when the initial products of hydrolysis and condensation of alkylchlorosilanes are oxidized by air at 200-300°C, the organic radical is detached from the silicon atoms, forming aldehydes or acids. The polyarylsiloxanes do not cleave the phenyl radical under such conditions, but when treated by treatment with strong hydrochloric acid at 170-180°C it has been possible to cleave the aryl radicals in the form of benzene, while aliphatic radicals are not cleaved by such treatment.
The heating of the initial products of hydrolysis and condensation leads to an increase in their viscosity and to the formation of infusible and insoluble resins.

The condensation of arylsilanols can also be accelerated by using dehydrating agents.

The polyphenylsiloxane waxes and resins have very high dielectric properties:

<table>
<thead>
<tr>
<th>Wax</th>
<th>Resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tangent of Dielectric Loss</td>
<td></td>
</tr>
<tr>
<td>Angle at 10^6 Cycles</td>
<td>0.0008 0.003</td>
</tr>
<tr>
<td>Dielectric Constant</td>
<td>2.6 3.1</td>
</tr>
</tbody>
</table>

The polyphenylsiloxane resins burn with a smoky flame forming carbon and SiO₂.

The phenyl radicals are not cleaved from the silicon by heating in air to 400°C for several hours. By chlorination of the aromatic nucleus in an arylchlorosilane, the properties of the polyphenylsiloxanes prepared from them may be sharply modified.

On the chlorination of phenyl dichlorosilane in the presence of catalysts, one or more chlorine atoms may be introduced into the phenyl radicals. The chlorophenyltrichlorosilane so obtained is then hydrolyzed, and the hydrolyzates are subjected to condensation by heating. In this case hard resins are formed which melt at a higher temperature than polyphenylsiloxanes, and have a higher resistance to fire. When three chlorine atoms are introduced into the phenyl nucleus, the product completely loses its combustibility.

The chlorinated polyphenylsiloxane resins possess a high resistance to oxidation. They are soluble in chlorinated hydrocarbons and other organic solvents, but their fusibility and solubility depends on the degree of condensation. These resins have excellent electrical properties, and the dielectric losses in them amount to only 3% at 200°C. Polytrichlorophenylsiloxane has a resistivity $P_v = 10^9$ ohms/cm. The dielectric constant increases with the chlorine content of the polymer, reaching 3.5 at 25°C for polytrichlorophenylsiloxanes.
The chlorophenylchlorosilanes after hydrolysis are easily condensed on heating (Bibl.72).

Method of preparing polychlorophenylsiloxane resins. Diphenyldichlorosilane is mixed with a catalyst (0.5% of iron powder or 0.1% of antimony pentachloride) and is chlorinated at 70-120°C until the gain in weight of the chlorinated product corresponds to the introduction of 6 to 10 chlorine atoms into the molecules. The product is distilled in vacuo. The chlorinated diphenyldichlorosilane is a solid substance. It is hydrolyzed by water without a solvent. Di-(chlorophenyl)-silanediol is a white flocculent mass which is separated and washed with water until all the acid is removed, and is then heated at 125-150°C until a colorless liquid is obtained. Further heating at 175-250°C, for not less than 1 hour, leads to the formation of a resin.

The chlorinated polyarylsiloxanes may be combined with organic resins and heat-resistant materials may be prepared in this way. These resins are easily and well plasticized. Pigmented with graphite, they are particularly suitable for coating metal pipes.

Atoms of fluorine, bromine, or iodine may be introduced into the aromatic groups. The polyfluorophenylsiloxanes are particularly interesting as heat-resistant resins for work at high temperatures.

The chlorosilanes used for preparing resins may contain chlorinated aryl radicals in combination with alkyl radicals. The polymethylchlorophenylsiloxanes, for instance, are of a certain interest; if the aryl radicals in them contain 3, 4, and 5 chlorine atoms, then such resins are fire-resistant.

Other polyarylsiloxanes, like the polyphenyl-, polyxylyl- and polynaphthylsiloxanes, are soluble vitreous brittle substances.

Polyditolylsiloxane resin prepared from ditolyldichlorosilane is a low-melting, hard, brittle substance soluble in acetones, hydrocarbons, and chlorinated hydro-
carbons. The high-polymer product of condensation of p-tolylsilanetriol is soluble in aromatic hydrocarbons.

The polyphenoxysiloxanes particularly are extremely important resinous products which may be prepared from the p-bromodiphenyl ester by the action of a Grignard reagent. The large size of the phenoxyphenyl radicals affects the rate of condensation. These products are condensed very slowly, and only prolonged heating converts the crystalline mass into high-polymer polysiloxanes. Polymers containing one phenoxyphenyl radical per silicon atom are hard, brittle resins of a brownish color, having high resistance to heat and good dielectric properties. These resins may be made fire-resistant by using organochlorosilanes with one or two chlorinated phenyl nuclei in their production.

Polyalkylarylsiloxane Resins

As already stated above, the polyalkylsiloxanes with a high R/Si ratio are oily liquids or elastic polymers, capable of polymerization on heating. These products possess good adhesive properties. The optimum R/Si ratio for polymethylsiloxane is 1.5, and for polybutyl- or polybenzylsiloxane, 1.0. Polyarylsiloxanes with high R/Si ratios are brittle, vitreous, soluble, and fusible products. This shows that, on the hydrolysis of arylhydroxysilanes, cyclic products which form three-dimensional molecules only with difficulty are formed. Polyarylsiloxane resins are too brittle for use as coatings or impregnating agents. Studies have shown that the properties of both types of resins may be combined by preparing them from monomers containing alkyl and aryl radicals attached to one and the same silicon atom, or by cocondensation of alkyl and aryl hydroxysilanes. The copolymer formed in the latter case contains alkyl and aryl radicals attached to different silicon atoms. The method of cocondensation makes it possible to obtain more elastic products and allows various proportions between the alkyl and aryl radicals to be selected. In this way products with highly graduated properties may be obtained. Such resins possess high elasticity, thermoplasticity, and mechanical strength. Certain poly-
alkylarylsiloxanes have a mechanical strength and hardness exceeding these characteristics for polyalkyl- or polyarylsiloxanes.

Preparation of polyalkylarylsiloxanes (Bibl. 73). The initial products obtained as a result of the hydrolysis of a solution of methylphenyldichlorosilane in toluene at 30-40°C are heated 30 minutes with 125°C to remove the toluene, and then for 12-25 minutes at 175°C. After such treatment a soft polymer is obtained, which softens on heating but does not melt. On further heating a hard product is formed.

The resins in which the R/Si ratio is close to 1.8, and the number of alkyl and aryl groups is the same, possess good elasticity, strength and infusibility in the polymerized state. A polymethylphenylsiloxane resin having about 1.00 methyl and 0.80 phenyl radicals per silicon atom has good dielectric properties; thus a film polymerized on glass fiber has a tangent of dielectric loss angle of 0.001 at 60 cycles, and a dielectric strength of about 32 kV/mm at 100°C. Such a resin without a filler (in the form of a hard disc) at the same temperature has only half these dielectric losses.

Polydimethylphenylsiloxane resin applied to glass fabric, after heating to 300°C for 300 hours, has a dielectric strength of about 40 kV/mm, which on further heating slowly decreases. After heating the resin for 340 hours, its dielectric strength is 20 kV/mm, and after 640 hours this decreases to a value approaching the value of the voltage necessary for an air breakthrough, which points to the presence of cracks in the film. These cracks cannot be detected by the naked eye. The dielectric properties and abrasion resistance of polymethylphenylsiloxane are somewhat better than those of polymethylsiloxane resins.

Polyethylphenylsiloxane resins are prepared, either directly from ethylphenyl dichlorosilane or phenylethylidithoxysilane, or by cocondensation of a mixture of hydrolyzates of diethyldichlorosilane with diphenyldichlorosilane or with diphenyl diethoxysilane. In the former case polymers are obtained in which the same silicon atoms are attached to different organic radicals, and the units of the molecular
chain have the following composition:

\[
\begin{array}{c}
\text{C}_2\text{H}_6 & \text{C}_2\text{H}_6 & \text{C}_2\text{H}_6 \\
\text{Si-O-Si-O-Si-O} \\
\text{C}_2\text{H}_6 & \text{C}_2\text{H}_6 & \text{C}_2\text{H}_6
\end{array}
\]

and in the second case, the following composition:

\[
\begin{array}{c}
\text{C}_2\text{H}_6 & \text{C}_2\text{H}_6 & \text{C}_2\text{H}_6 \\
\text{Si-O-Si-O-Si-O} \\
\text{C}_2\text{H}_6 & \text{C}_2\text{H}_6 & \text{C}_2\text{H}_6
\end{array}
\]

The properties of the resins prepared by the first and second scheme differ considerably from each other. The resins corresponding in structure to those prepared by the first scheme are more elastic than those prepared by the second scheme for one and the same average molecular weight and number of phenyl and ethyl radicals to a silicon atom. However, the polymers of both the first and second type do possess higher elasticity than the compounds containing only phenyl radicals.

When resins are prepared from the hydrolysates of phenylethylidichlorosilane (Bibl.74), and, in particular, when triethyltriphenylcyclotrisiloxane is heated and the oxygen of the air is passed through it, oxygen bonds are formed between two or more rings. Polymers containing two or three rings are oily liquids; polymers containing a larger number of rings have a high viscosity and are resinous substances.

Oxygen bonds may be formed either by oxidation or by the action of catalysts. Alkyl radicals are usually replaced by oxygen atoms by means of oxidation, while aryl radicals are more easily cleaved during hydrolysis in the presence of a catalyst, strong HCl, a small amount of ferrous chloride, aluminum chloride, or zinc chloride. The two reactions may proceed simultaneously. Thus, for example, for the formation of intermolecular oxygen bonds in polyethethylsiloxanes, with substitution of the alkyl radical, the polymer is heated to 200-300°C while air is passed.
through it. The liberation of acetaldehyde in this case shows that the ethyl radicals are gradually oxidized and replaced by oxygen. The reaction may be represented as follows:

$$
(n + 2)C_4H_8 - Si-O-Si-C_4H_8 + 4(n + 1)O \rightarrow \\
O-Si-O
$$

$$
\cdot C_4H_8 - Si-O-Si - \left[ O-Si-O-Si \right] - O-Si-O-Si-C_4H_8 + \\
O-Si-O
\cdot C_4H_8 - C_4H_8
\cdot O-Si-O
\cdot C_4H_8 - C_4H_8
+ 2(n + 1)CHCHO + (n + 1)H_2O
$$

During the reaction the viscosity increases, and after a few hours of heating at the above temperatures, the substance becomes very viscous and tacky. At higher temperatures, the reaction proceeds more rapidly, but a considerable loss of the product is observed owing to its volatilisation. If the heating of the viscous mass is continued while air is vigorously passed through it, it hardens, and forms an elastic, non-tacky, infusible and insoluble substance. This modification of its properties is due to the formation of cross-links and to side-branching owing to the oxidation of the ethyl radicals. The modification of the properties may perhaps also be connected with the formation of cyclic polymers of high molecular weight.

To form intermolecular oxygen bonds by removal of the aryl radicals, polyphenylethylsiloxane is heated to 170-180°C under slow dropwise addition of a solution of HCl to the reaction mass. The presence of traces of ferrous chloride in the acid increases the velocity of the reaction. During the reaction benzene is liberated, and the viscosity of the product gradually increases, indicating the cleavage of phenyl radicals and the formation of Si-C-Si linkages. Such a reaction may be represented by the following scheme:
If the heating at 170-180°C is continued in the presence of HCl, then the substance becomes viscous and tacky after a few hours. In this state, it still remains soluble in toluene. Further heating to a higher temperature converts the product into a resinous, elastic, nonadhesive, insoluble and infusible polymer. When ferrous chloride is used as a catalyst, the time necessary for the transition of the polymers into the insoluble state is considerably shortened. In case of need, the combined reaction may be conducted by heating an arylalkylchlorosilane, for instance phenylethyldichlorosilane, to 170-180°C for a few hours, simultaneously passing moist air and HCl through the liquid. In this case the oxidation of the ethyl radicals by the oxygen of the air, and the cleavage of the phenyl radicals as a result of the hydrolysis due to the presence of HCl, both take place.

Another method of simultaneous removal of alkyl and aryl radicals consists in treating the initial hydrolyzates with nitric acid, which cleaves the alkyl radicals as a result of oxidation, and the aryl radicals as a result of nitration and hydrolysis. Nitrobenzene is obtained as a byproduct.

The results of analysis and molecular weight determinations show that the resins, in the soluble stage of polymerization, consist of linear polymers with an average of four heterocyclic rings in the molecular chain, which are shown above in eq.(1) and eq.(2), with a degree of polymerization equal to not less than 2. The polymer obtained by heating phenylethyldichlorosilane in the presence of an HCl solution and of air contains, according to the analytical results, 19.5% of silicon.
oxide and 50.6% of carbon. Its molecular weight is 1310. In a polymer whose structure corresponds to eq. (2), for \( n = 2 \), and for molecular weight 1386, the \( \text{SiO}_2 \) content should be 51.9% and the carbon should be 51.9%. A polymer with the structure corresponding to eq. (1) for \( n = 2 \) should contain 43.0% of silicon oxide and 60.2% of carbon, and its molecular weight would be 167%. On subsequent, more prolonged polymerization, the size of the molecules is increased owing to addition of more heterocyclic rings.

On hydrolysis of a mixture of phenyltrichlorosilane and phenylethyltrichlorosilane in the proportion of 1:2 by water, followed by heating of the hydrolyzate to 170°C by the above method, a viscous and thermoplastic polymer is obtained, possessing almost the same properties as the polymer prepared by similar treatment of phenylethylidichlorosilane alone.

It may be postulated that the dehydration of the mixture of intermediate hydroxy-polyalkylarylsiloxanes leads to the formation of chains consisting of heterocyclic rings similar to those we have just described. In this way there would be no need for complete removal of the phenyltrichlorosilane from the phenylethylidichlorosilane. As a rule, in the presence of phenyltrichlorosilane, harder and more brittle resins are formed, since in this case the transition from the stage at which they are rubberlike and flexible to the stage of complete hardening, proceeds more rapidly.

The high-polymer ethylphenylsiloxane resins have good dielectric and mechanical properties, but they withstand heating in air only to a somewhat lower temperature than the polymethylphenylsiloxane resins. The ethyl radicals are more easily oxidized at high temperatures than methyl radicals are.

**Mixed Organic and Organosilicon Resins**

A considerable number of studies have been devoted to the preparation of mixed organic and organosilicon resins. These investigations, for the most part, have been directed towards the development of methods of cocondensation of monomeric or
polymeric organosilicon compounds with organic resins or other high-polymer compounds. USSR chemists have prepared cocondensation products of polyester resins with esters of orthosilicic acid (Bibl.76); of phenol-formaldehyde resins with esters of orthosilicic acid; of resins from the condensation products of urea with formaldehyde and tetraethoxysilane and its hydrolyzates (Bibl.78); and cocondensation products of aniline-formaldehyde resins with the hydrolyzates of tetraethoxysilane (Bibl.79). By the condensation of pentaphthalic resins, as well as of other types of glyptal resins with esters of orthosilicic acid and their hydrolyzates, resins used in the manufacture of paint coatings have been prepared (Bibl.80). The combination of nitrocellulose with esters of orthosilicic acid has led the formation of modified nitrocellulose lacquers (Bibl.81). The reesterification of castor oil by esters of orthosilicic acid has yielded liquid cocondensates of the plasticizer type (Bibl.82).

The products of the cocondensation of the ethyl ester of orthosilicic acid with organic resins have been described by G.S. Petrov and A.P. Kreshkov (Bibl.83). These products are of a definite practical interest. R.M. Erastova (Bibl.84) has made studies, in order to prepare lacquers, of the introduction of esters of orthosilicic acid into the fatty oils and glyptal resins.

The use of the esters of orthosilicic acid (ethyl-silicates) as film-forming substances both independently and in combination with other organic resins has been studied (Bibl.85).

The pigments that are most suitable for such lacquers are titanium oxide, venetian red, black ilmenite, golden ochre, cadmium yellow, cobalt blue, burnt umber, and chrome green. Mixing of the active pigments, such as zinc oxide or aluminum with ether immediately before use is recommended. The process of hardening the paint consists in the complete hydrolysis of the ester of orthosilicic acid under the action of the moisture of the air.

The pigment is ground in an organic solvent, alcohol or benzene, and the paste
so obtained is mixed with ethyl silicate. To prepare a lacquer, definite weight proportions of the paste and ethyl silicate are taken. Paints on an ethyl silicate base are used as fire-protective coatings, in the building industry, and other fields. They form a porous film which is compatible with wet stuccoing, and is easily wetted. Such paints are hard to apply to a surface covered with an oil lacquer. The combination of ethyl silicate with other forms of artificial resins considerably improves the properties of the coatings. A mixture of ethyl silicate with a phenol-formaldehyde resin forms a film resistant to strong acid and alkalies. Such a mixture is obtained by boiling a solution of a phenol resin with ethyl silicate in benzene solution. When equal parts by weight of the above resin and tung oil are boiled 30 minutes, a lacquer is formed that can be well pigmented with aluminum powder. Ethyl silicate may also be used for the modification of glyptals. In this case, the mono- and diglycerides of linseed oils are boiled with ethyl silicate, leading to the formation of a resin similar to the glyptals, but with improved properties.

The esters of the higher alcohols and orthosilicic acid, when combined with glyptals or cellulose esters, form films with better properties than when ethyl silicate is used.

The combination of ethyl silicate with cellulose esters increases the tensile strength and flexibility of the films. Such films possess good adhesion to glass, by comparison with unmodified nitrocellulose films. The lacquer is prepared by dissolving nitrocellulose in butyl acetate. The solution so formed is thinned with toluene, and dibutyl phthalate in an amount equal to 50% of weight of the dry nitrocellulose is added to it as a plasticizer, followed by the addition, for the same purpose, of ethyl silicate in an amount equal to 85% of the weight of the dry nitrocellulose.

The esters of orthosilicic acid in the partially hydrolyzed form has found application in combination with the polyvinyl resins. A mixture of ethyl silicate and tricresyl phosphate is a good plasticizer, which reduces the thermoplasticity of
polyvinyl chloride.

Partially hydrolyzed ethyl silicate and other organosilicon polymers may modify such resins as poly(methyl methacrylate), polyvinyl chloride, polyvinyl acetate, polyethylene, polystyrene, polyvinylbutyral, polyvinyl alcohol, neoprene, unvulcanized rubber, chlorinated rubber, nylon, cellophane, acetylcellulose, ethylcellulose and polyamides (Bibl.86, 87).

For modification of polyvinyl acetate, ethyl silicate is partly hydrolyzed to a content of 0.1-0.7 ethoxy groups per silicon atom, and is mixed with an alcoholic solution of polyvinyl acetate, partially hydrolyzed (from 5 to 30%), in a ratio of 1 : 2-6 of SiO₂ in the polymer.

The films obtained from resins modified with ethyl silicate have a high degree of hardness, resistance to the atmosphere, good adhesion to metal, elasticity, and resistance to aging. The coatings may be dried either by the hot or the cold method.

Alkyd and alkyd-oil resins and alkyd-butyric resins are subjected to cocondensation with organohydroxysilanes, forming heat-resistant resins for coatings (Bibl.82, 89).

These resins are prepared by the following method.

A mixture of 50 parts by weight of resyl glyptal, containing 4.2% of oil, and having an acid value not over 40-47, and 110 parts by weight of a 53% of the hydrolyzate of phenyltrichlorosilane in xylene is heated under a reflux condenser for 1-1.5 hours at 132°C. 0.7 parts weight of water is liberated. After the boiling, 10 parts by weight of butanol is added to the mixture.

A film of this lacquer hardens at 150°C in 0.5-1 hour into a hard, flexible, material with exceptional resistance to chemicals. A white enamel from such a lacquer withstands high temperatures.

Resins suitable for coatings and for plastics are prepared by combining tetrafurfuryloxysilane or tetramethylaryloxysilane with alkyd resins (Bibl.90). The tetrafurfuryloxysilane is prepared by reesterification of tetraethoxysilane with
Preparation of tetrafururyloxysilane for modification of alkyd resins. A mixture of 1176 parts by weight of furfuryl alcohol is mixed with 312 parts by weight of tetraethoxysilane and 1.2 parts by weight of lead oxide, and is heated on an oil bath. During the heating, 240 parts by weight of distillate are distilled off, and are returned to the reaction vessel. Xylene, 520 parts by weight, is also added to it. The temperature of the bath is raised to 145°C, and 373 parts by weight of a distillate boiling below 83°C is distilled off. This distillate contains 262 parts by weight of ethanol. The residue in the flask is distilled in vacuo in a stream of CO₂, and a fraction boiling at 204-205°C (3 mm) is collected. Redistillation yields 400 parts by weight of tetrafururyloxysilane, boiling point 201-206°C (4 mm). Recrystallization from a mixture of toluene and petroleum ether yields a product melting at 38-39°C. A solution of glyptal, modified with tung oil or fish oil, is mixed without heating with 2% by weight of tetrafururyloxysilane. Films of the products based on this are dried at 100°C and are more frost resistant than films of the glyptal prepared without tetrafururyloxysilane.

Tetramethylallyloxysilane is prepared from a mixture of 460 parts by weight of tetraethoxysilane and 1200 parts by weight of methallyl alcohol. A small piece of metallic sodium is added to the reaction mixture, and the mixture is then heated under a reflux condenser to boiling. The temperature in the upper part of the condenser is held within the limits of 78-80°C, in order to be able to distill all the ethanol liberated during the reesterification and to collect it in the receiver. After distillation of the theoretical quantity of ethanol, the excess of methallyl alcohol is distilled off, and the residue is fractionated in vacuo. The tetramethylallyloxysilane boils at 128-130°C (6 mm). It is added, 5% by weight, to glyptals to modify them.

As a result of addition of tetramethylallyloxysilane to glyptals, harder and stronger films than films of the glyptal resin alone are obtained.
Copolymerization of unsaturated esters of boric or orthosilicic acid with vinyl and vinylidene derivatives is conducted by the usual method, in the presence of benzoyl peroxide or butyl peroxide, in a solvent or without it (by the block method).

1. A solution of 40 parts by weight of methoxymethyl methacrylate, 10 parts by weight of a tetramethylaryloxylysilane, and 0.1 parts by weight of benzoyl peroxide is polymerized at 65°C, forming a transparent soft polymer having a high adhesion to glass.

2. A mixture of 90 parts by weight of methyl methacrylate and 10 parts by weight of a tetramethylaryloxylysilane is heated under a reflux condenser until a viscous liquid is formed. This product, applied to glass, and then polymerized again at 65°C (toward the end at 95°C), forms a good film possessing high adhesion and water resistance.

The properties of the copolymers depend on the proportions of the components. When the amount of unsaturated allyloxylysilane or borate is increased, the softening point of the polymers is lowered.

Polyorganosiloxane Elastomers

The polyorganosiloxane elastomers are linear polymers whose molecules have the following initial structure:

\[
\begin{array}{cccc}
R & R & R & R \\
-\text{Si-O-Si-} & -\text{Si-O-Si-} & -\text{Si-O-Si-} & -
\end{array}
\]

After the proper heat treatment, the linear polymers are cross-linked by the transverse bonds that are formed:

\[
\begin{array}{cccc}
R & R & R & R \\
-\text{Si-O-Si-} & -\text{Si-O-Si-} & -\text{Si-O-Si-} & -
\end{array}
\]
The elastic properties and the elasticity of the elastomers depend on the number of -Si-O- units in the molecular chain and on the number of cross-links. The higher the average molecular weight of an elastomer, the higher its elasticity and mechanical strength. The presence of an insignificant number of cross-links in polymers favors the increase of the elastic properties of an elastomer and increasing its mechanical strength. In the presence of a large number of cross-links, the polymer loses its elastic properties.

The character and molecular weight of the organic radicals making up the polymeric molecule exert a great influence on the properties of elastomers and on the course of their formation.

The exceptional resistance of polyorganosiloxane elastomers to heat, and their insensitivity to the action of oxygen is explained by the nature of the siloxane bond. The strength of the siloxane bond is 89.3 kcal/mol, which is considerably more than the strength of the carbon-carbon bond, which is 62.77 kcal/mol. It is this fact that is responsible for the considerably higher thermal stability of polyorganosiloxane elastomers by comparison with the stability of the organic natural and synthetic rubbers. The absence of unsaturated bonds in the polyorganosiloxane elastomers and the stability of the Si-Carbon-silicon bond, owing to its screening by a silicon atom, assures it of low sensitivity to the action of oxygen.

As remarked above, the presence of cross-links between the linear molecules in elastomers is of substantial importance. The formation of such cross-links can be accomplished either by introduction of trifunctional and tetrafunctional monomers into the polymer during condensation and polymerization, or by oxidizing the organic hydrocarbon linear polymers.

The introduction of considerable amounts of tri- or tetrafunctional compounds leads to the formation of low-elasticity products owing to the great number of
cross-links formed in this case. Consequently, the adjustment of the proportions between the bifunctional and polyfunctional monomers has a great influence on the elastic properties of the polymer.

The alkyl- and arylhydroxysilanes have a tendency to form larger rings, and their tendency to cyclization is more strongly manifested, than in the corresponding carbon compounds. This interferes with the formation of linear polyorganosiloxanes.

A dialkyldihalosilane of a high degree of purity serves as the starting monomeric compound for the preparation of a linear polymer of high molecular weight. Even insignificant admixtures of the trialkylhalosilanes will sharply reduce the molecular weight of the polymer. For instance, the presence of only an insignificant admixture of $R_2SiCl$ (1-mol% per mol of $R_2SiCl_2$) will limit the degree of polymerization of the polymer to 200 $R_2SiO$.

The presence of an admixture of traces of the alkyltrichlorosilane in the dialkyldichlorosilane leads to the formation of polymers of branched structures, and, in a number of instances, to the gelation of the hydrolyzate. If the trialkylchlorosilane and the alkyltrichlorosilane are present in appreciable amounts in the dialkyldichlorosilane, then the polymer formed will be characterized by the presence of cross-links between the short chains (Bibl.86). Thus the degree of purity of the monomeric compounds is of extreme importance in the production of linear polysiloxanes.

It is well established today that linear polyorganosiloxanes of very high molecular weight can be produced.

The polyorganosiloxane elastomers that were first prepared had a low tensile strength and a low elasticity. They were brittle gels, and were more viscous than elastic substances. The relatively poor mechanical properties of the polysiloxane elastomers that were prepared during the early period of research is explained by the inadequate purity of the starting monomeric compounds. The poor mechanical properties were due to the high polydispersion of the product and to its consider-
able content of low-molecular substances. The polyorganosiloxane elastomers produced today far excel the first specimens in mechanical strength, and this fact encourages their widespread use. The possibilities in this field are still far from completely utilized, and it may be expected that polyorganosiloxane elastomers of mechanical strength no lower than that of the organic elastomers will be prepared.

By the fractionation of a polydimethylsiloxane elastomer from a mixture of acetone and ethyl acetate, it was possible to separate fractions of the following molecular weight, osmometrically determined:

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$2.8 \times 10^6$</td>
</tr>
<tr>
<td>2</td>
<td>$1.5 \times 10^6$</td>
</tr>
<tr>
<td>3</td>
<td>$6.1 \times 10^6$</td>
</tr>
<tr>
<td>4</td>
<td>$2.8 \times 10^6$</td>
</tr>
</tbody>
</table>

Fraction 5 was a viscous liquid (Bibl.87).

A polyethylsiloxane elastomer, on fractionation from an alcohol-benzene mixture, was separated into fractions of average molecular weight, viscosimetrically determined, ranging from 1600 (liquid product) to 45,000 (elastic substances) (Bibl.86).

A study of the variations in the dimensions of specimens of polyalkylsiloxane elastomers at low temperatures showed that there exists a narrow temperature interval within which the dimensions of the specimen vary sharply. This interval corresponds to the temperature of crystallization of the polydimethylsiloxane elastomers.

On further cooling of this specimen, a region of sharp variation of the dimensions of the specimen is again observed. This region corresponds to the second-order transition point (vitrification temperature) of polyalkylsiloxane elastomers.

Figure 53 shows the behavior of polyalkylsiloxane elastomers on cooling and heating. Crystallization is observed between $-60^\circ C$ and $-67^\circ C$. This temperature limit of crystallization has been found for various specimens of elastomers. The crystallization of polyorganosiloxane elastomers is more rapid than that of natural...
rubbers. Melting begins a few degrees above the crystallization point and ends around \(-39^\circ C\). The value of the volume change connected with the crystallization of polyalkylsiloxane elastomers ranges from 2.0 to 7.8%. The maximum volume change on crystallization of natural rubbers is about \(3\%\) (Bibl.88).

If specimens of polyalkylsiloxane elastomers are alternately cooled and warmed at a temperature somewhat above \(-60^\circ C\), neither crystallization nor melting will be observed. The results of experiments conducted at temperatures between \(-30^\circ C\) and \(-50^\circ C\) are shown in Fig.54.

If crystallization proceeds at a measurable rate in this temperature range, the length of the specimen will successively decrease as a function of the temperature.

Figure 55 shows the dimensional variation of specimens of polyalkylsiloxanes elastomers at various temperatures.

The second-order transition point corresponds to the point of inflexion of the slope of the curves and is entirely determinate for all the specimens.

It will be seen from Fig.55 that the second-order transition point for polydimethylsiloxane elastomers is at \(-123^\circ C\). This temperature is considerably lower than the second-order transition point for organic polymers.

The transition point of polymethylsiloxanes does not vary when a filler is added, or on vulcanization. This behavior of polymethylsiloxane elastomers differs from the behavior of natural rubbers, in which a filler and vulcanization change the transition point.
Observation of this specimen of elastomers during warming and cooling showed that while a normal second-order transition is observed at 103°C, crystallization, supercooling, and melting on warming, both at higher temperatures. Crystallization on supercooling occurs at around -75°C, and the end of melting, on warming, at a temperature of about -15°C. It is probable that the crystallization point is in the range from -75°C to -100°C. Such behavior of the polydimethylsiloxane elastomers resembles that of the natural rubbers, which likewise may be supercooled and crystallized in a definite temperature range.

Polyalkylsiloxane elastomers without a filler have a very high coefficient of expansion, which is equal to $120 \times 10^{-5}$ (at temperatures between -35°C and 0°C), that is, considerably greater than that of most organic polymers. The coefficient of expansion of elastomers decreases on the introduction of a filler.

Fig. 54 - Temperature Dependence of the Relative Expansion of Polydimethylsiloxane Elastomer:
1 - Cooling of elastomer; 2 - Warming of elastomer
a) Temperature, °C; b) Relative expansion, μ/cm

Fig. 55 - Temperature Dependence of Relative Expansion of Polydimethylsiloxane Elastomer in the Range from -90°C to -170°C:
1 - Polydimethylsiloxane elastomer;
2 - The same elastomer with filler;
3 - Vulcanized polydimethylsiloxane elastomer with filler
a) Temperature, °C; b) Relative expansion, μ/cm
The mechanical properties of polysiloxane elastomers are considerably inferior to those of natural and synthetic rubbers. The tensile strength of a polydimethylsiloxane elastomer without a filler is 10-25 kg/cm², and with a filler it is 30-45 kg/cm². The strength of individual specimens of the elastomer with a filler is as high as 80 kg/cm². Specimens prepared in the laboratory with the special filler JS-1995 with a strength (Bibl.89) of about 130 kg/cm² (cf. Table 97) (Bibl.89), have been described.

Titanium dioxide is the most heat-resistant filler for polydimethylsiloxane rubbers. Carbon black at 200°C gives off volatile products, thus forming bubbles in the rubber. The problem of improving the properties of materials from polysiloxane elastomers is related not only to the improvement of the properties of the elastomer, but also to the selection of the proper heat-resistant filler, and of its disperseness. The strength of polydimethylsiloxane rubbers varies from 5 to 30 kg/cm² with a variation in the temperature from -50°C to +200°C, and the Shore hardness from 70 to 85. At elevated temperatures the phenomenon of creep is observed. Polymethylsiloxane elastomer remains elastic at a temperature of -65°C. It has a high adhesion to glass, which is greater than the strength of the resin itself.

The swelling of polydimethylsiloxane rubbers depends on the amount of filler and on the type of solvent. The minimum swelling at 20°C after 72 hours is observed in water (3% increase in volume); in acetone the swelling is about 11%, in mineral oil 8%. Benzene, isooctane, and CCl₄ cause strong swelling of the elastomer (up to 100-120%).

It is interesting to note that specimens of the elastomer filled with glass fabric to 10% of the total volume, swell 50-80% less in the strongly acting solvents, benzene and carbon tetrachloride, than the specimens without the glass fabric.

The electrical and mechanical properties of polydimethylsiloxane elastomer vary only slightly over the wide temperature range from -63°C to 200°C.

The properties of polydimethylsiloxane rubber with powder filler, and also that
Polymethyl disiloxane Rubbers with Ja-1995 Filler

<table>
<thead>
<tr>
<th>Volume of pigment</th>
<th>Perbenzoate %</th>
<th>Hardening in Thermostat</th>
<th>Tensile strength</th>
<th>Elevation %</th>
<th>Shore hardness</th>
<th>Compressive strength %</th>
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<tbody>
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<td></td>
<td>hrs</td>
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<td>205</td>
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<td>613</td>
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<td>1</td>
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<td>118.0</td>
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<td>61</td>
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<td>118.0</td>
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<td>62.9</td>
<td>275</td>
<td>89</td>
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</tbody>
</table>

of polydimethylsiloxane rubber with a glass-fabric filler, are as follows.

<table>
<thead>
<tr>
<th>Elastomer with Powder Filler</th>
<th>Elastomer with Glass Fabric</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength, kg/cm²</td>
<td>25.0</td>
</tr>
<tr>
<td>Elongation, %</td>
<td>225</td>
</tr>
<tr>
<td>Sorption of Water in 100 Hours, %</td>
<td>2.7</td>
</tr>
<tr>
<td>Resistance to Action of Ozone</td>
<td>Excellent</td>
</tr>
<tr>
<td>Dielectric Constant at 1000 Cycles</td>
<td>3.07</td>
</tr>
<tr>
<td>Breakdown Voltage at 60 Cycles, kv/mm</td>
<td>15-25</td>
</tr>
</tbody>
</table>

It will be seen from these data that the material prepared by a combination of elastomers with glass fabric has a considerably higher strength, but lower dielectric
indices, than the elastomer with powder filler.

In the electrical breakdown of the specimens and the action of the arc discharge on the surface of the specimen, no carbonation or formation of conducting coke bridges is observed. As a result of electrical breakdown, silicon oxide, which is a good dielectric, is formed.

After 50 days of heating of specimens of polydimethylsiloxane elastomer at 200°C, their flexibility is diminished, but they can still be bent 180° without breaking. The loss of weight of the specimen in this case is 2.5%, and the shrinkage is 1.7%. On further heating of the elastomer, its properties continue to vary very slightly. After 90 days at 200°C, the loss of weight is about 1.2%.

After 50 days of heating of 250°C, all the specimens of elastomer remain sufficiently flexible and permit a 180° bend without the appearance of cracks. The losses in weight in this case amount to 6.3% and the shrinkage to 4.0%. After 50 days of heating of the specimens at 300°C, they become brittle and form cracks on bending. Heating for 42 days under these conditions still does not lead to brittleness, and the specimens can be bent 180°. The loss in weight of the specimens after 42 days of heating at 300°C is 11%, the shrinkage is 7.1%. The presence of zinc oxide in the elastomer as a filler increases the weight losses during heating.

Polymethylsiloxane elastomer is used to manufacture gaskets and other articles used for work in a wide range of temperatures from -50°C to +200°C.

**Thermal Oxidative Degradation of Polvorganosiloxanes**

The thermal stability of polyorganosiloxanes is the fundamental characteristic which determines the limiting temperatures at which the various polymers of this class can be used. In this connection it is important to establish the influence of structure on thermal degradation and the mechanism of such degradation itself. The various organic radicals or groups making up the polymer molecules, and the number of these radicals or groups, undoubtedly must affect the thermal stability of polyorganosiloxanes. For this reason the study of the influence of the chemical nature...
of the radical or group on the thermal stability of the polyorganosiloxanes allows a number of regularities of great practical importance to be established.

The variation of the number of radicals or groups in polyorganosiloxanes is associated not only with the quantitative variation of the content of the organic portion, but also with the fact that when the number of radicals attached to a silicon atom changes from two to one, the structure of the polymer molecule also changes from linear to three-dimensional. This would likewise affect the thermal stability of the polymers as well.

The literature contains fragmentary data on the thermal stability of certain liquid polyorganosiloxanes; it is stated that the polydimethylsiloxane liquids are stable up to 175°C, and the polyphenylmethylsiloxane liquids (Bibl.90) up to 250°C. With respect to the solid polymers, only the fact that the polymethylsiloxanes decompose at considerable velocity at 300°C is known (Bibl.91). The polydimethylsiloxanes decompose at 400°C in vacuo, forming liquid cyclic low-molecular compounds (Bibl.92).

We shall now consider thermal oxidative degradation of polydiorganosiloxanes with linear structure of the molecular chains and of polyorganosiloxanes with three-dimensional structure of those chains, of various compositions; polymers with strongly developed surface area (ground to the powder state) were subjected to degradation at temperatures of 250°C, 350°C, 450°C and 550°C.

**Degradation of Polydiorganosiloxanes**

The degradation of polydiorganosiloxanes was studied on the example of the linear polymer obtained by hydrolysis of dimethyldichlorosilane by water:

\[
\text{nR}_2\text{SiCl}_n + n\text{H}_2\text{O} \rightarrow \left[ \begin{array}{c} \text{R} \\ \text{Si} \\ \text{O} \\ \text{R} \end{array} \right]_n + 2n\text{HCl}
\]
Studies showed that polydimethylsiloxane at 250°C undergoes only slight degradation (Fig.56), but that at 300°C intense cleavage of the polymer takes place; in this case elementary units become detached from the molecular chain. Deeper degradation with a rupture of the chains at the Si–O bond is sharply manifested at 400°C.

![Graph](image1)

Fig.56 - Relation of the Degree of Degradation (in % of weight loss) of Polydimethylsiloxane to the Temperature, and to the Duration of Heating
a) Time, hours; b) Loss of weight, %

In this case the weight loss of the polymer exceeds the losses theoretically possible corresponding to the detachment of methyl groups alone (the dashed line in Fig.56).

The treatment of polydimethylsiloxane with benzoyl peroxide, which leads to the conversion of linear molecules into cross-linked molecules owing to the formation of oxygen bridges between the chains of the linear molecules, increases the thermal stability of polydimethylsiloxane (Fig.57).

Chemical analysis of the polymers after heating them at various temperatures (Table 98) shows that at 300°C the number of CH₃ groups in polydimethylsiloxane
diminishes appreciably after 5 hours \((C/Si = 1.74\) instead of 2.0) while the \(H/C\) proportion in this case is 3.07. At 350°C, the \(C/Si\) ratio sharply decreases (after 5 hours of heating it decreases from 2.0 to 0.32) but \(H/C\) not only fails to decrease but even increases somewhat; the same increase is also observed at 400°C.

Table 98

<table>
<thead>
<tr>
<th>Conditions of Degradation</th>
<th>Weight Loss %</th>
<th>Elementary Composition, %</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>[(CH₂)₅SiO]₈       (Starting Polymer)</td>
<td>-</td>
<td>32.44</td>
<td>8.13</td>
</tr>
<tr>
<td>1½ hrs at 300°C</td>
<td>15.0</td>
<td>32.71</td>
<td>8.25</td>
</tr>
<tr>
<td>5 hrs at 300°C</td>
<td>29.6</td>
<td>30.92</td>
<td>7.74</td>
</tr>
<tr>
<td>1 hrs at 350°C</td>
<td>28.66</td>
<td>33.86</td>
<td>7.36</td>
</tr>
<tr>
<td>2 hrs at 350°C</td>
<td>27.33</td>
<td>37.33</td>
<td>6.96</td>
</tr>
<tr>
<td>5 hrs at 350°C</td>
<td>23.19</td>
<td>23.19</td>
<td>6.11</td>
</tr>
<tr>
<td>0.5 hrs at 400°C</td>
<td>35.0</td>
<td>5.80</td>
<td>2.26</td>
</tr>
<tr>
<td>3 hrs at 400°C</td>
<td>42.0</td>
<td>15.35</td>
<td>4.54</td>
</tr>
<tr>
<td></td>
<td>60.5</td>
<td>1.54</td>
<td>0.99</td>
</tr>
</tbody>
</table>

These data show that the thermal oxidative degradation in linear polyorganosiloxanes takes place both by the rupture of the Si-C bond and by the rupture of the Si-O bond. The increased hydrogen content in the polymer after its heating corresponds to the temperatures at which a sharp fall in the carbon content is noted; this indicates the formation of hydroxyl groups at the silicon atoms in the polymer at the place of the detachment of the radicals. The hydroxyl groups are preserved, since their interaction is hindered by their low concentration and by the low mobility of the polymer molecules.

Degradation of Polymonoorganosiloxanes

The polymonoorganosiloxanes prepared by hydrolysis of alkyl- or aryltrichlorosilanes by water according to the formula:
$$nRSiCl_3 + 3nH_2O \rightarrow \left[ \begin{array}{c}
R \\
-\text{O-Si-O-} \\
\text{Si} \\
\text{O} \\
\text{Si} \\
\text{Si} \\
\text{O} \\
\text{Si} \\
\end{array} \right] + 3nHCl$$

where $R = \text{CH}_3, \text{C}_2\text{H}_5, \text{CH}_2 = \text{CH}, \text{C}_6\text{H}_5, \text{ClC}_6\text{H}_4, \text{Cl}_2\text{C}_6\text{H}_3, \text{Cl}_3\text{C}_6\text{H}_3, \text{or FC}_6\text{H}_4,$ were subjected to degradation.

The action of a high temperature on three-dimensional polymers with the structural unit $(RSiO_{1.5})_x$ causes various chemical transformations, mainly connected with the detachment of the organic radical from the silicon, that is, with the rupture of the Si-C bond without rupture of the main molecular chains at the Si-O bond. This will be seen from Fig. 58, showing the thermal oxidative degradation of polymethylsilsiloxane at 250°C, 350°C, 450°C and 550°C. Table 99 gives the result of analysis of the polymer after such degradation.

![Fig. 58 - Temperature Dependence of the Degree of Degradation (in Percentage Weight Loss) of Polymethylsilsiloxane and Duration of Heating](image)

a) Time, hours; b) Weight loss, %

It will be seen from these data that polymethyldisilsiloxane loses about 2.76% in weight after 24 hours at 250°C, but its elementary composition remains almost the same. Only at 350°C does a sharp rise in the weight loss begin (6.02% in 2 hours), accompanied by a drop in the C-Si ratio in the polymer to 0.47 instead of the original 1.0. The degradation proceeds by detachment of the methyl radical, as is indicated by the ratio $H/C = 2.93$ in the polymer after its heating. At 450°C, polymethylsilsiloxanes is more completely degraded, but even at this temperature, after 24 hours of heating, a certain amount of carbon still remains in the polymer, the C/Si
ratio remains equal to 0.1.

Table 99
Analysis of Polymethylsiloxane after Thermal Degradation

<table>
<thead>
<tr>
<th>Conditions of Degradation</th>
<th>Weight Loss %</th>
<th>Elementary Composition, %</th>
<th>Ratio</th>
<th>Number of OH groups</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
<td>Si</td>
<td>H/C</td>
</tr>
<tr>
<td>24 hrs 250°F</td>
<td>2.76</td>
<td>19.12</td>
<td>4.73</td>
<td>40.73</td>
</tr>
<tr>
<td>24 hrs 250°F</td>
<td>2.30</td>
<td>17.46</td>
<td>4.57</td>
<td>42.49</td>
</tr>
<tr>
<td>24 hrs 350°F</td>
<td>6.02</td>
<td>8.63</td>
<td>2.07</td>
<td>42.68</td>
</tr>
<tr>
<td>24 hrs 450°F</td>
<td>12.29</td>
<td>2.11</td>
<td>1.07</td>
<td>45.83</td>
</tr>
</tbody>
</table>

These data show that the complete removal of the carbon, that is, the rupture of the Si-C bond in polymethylsiloxane involves considerable difficulties. These difficulties arise from the fact that on thermal oxidative degradation, together with the detachment of the methyl groups, there is also a formation of oxygen bridges between the silicon atoms, which hinders the attack of oxygen on the methyl group (steric effect).

The experimental data show that the degradation of polymethylsiloxanes proceeds only on account of the detachment of the methyl radical (polymethylsiloxane after heating contains one methyl group to 10 silicon atoms), and that there is no rupture of the Si-O bonds in this case.

![Fig. 59 - Degree of Degradation (in Percentage Weight Loss) of Polyethyl-disiloxane, Related to Temperature and Duration of Heating](image)

a) Time, hours; b) Weight loss, %

The number of hydroxyl groups in the polymer after heating at 350°C and 450°C.
decreased to half its initial level, but it is still more than in polymethylsiloxane heated at 250°C. The presence of a considerable number of hydroxyl groups in polymethylsiloxane heated to temperatures at which the intense detachment of methyl groups from the silicon atom takes place shows that this process is accompanied by the formation of hydroxyl groups.

The thermal oxidative degradation of polyethyldisiloxanes at the same temperatures proceeds more intensely; at 250°C, a considerable cleavage of ethyl groups is noted (Fig.59).

After heating for 6 hours at 450°C, the specimen consisted of 99.0% SiO₂, and contain no carbon at all.

Polyphenylsiloxane has a high resistance to heat (Fig.60) at 250°C, 350°C and 450°C. Polyvinylsiloxane is distinguished, in comparison with the polyalkylsiloxanes, by its resistance to thermal degradation. This polymer (Fig.61) after heating at 350°C has only slight weight losses. Specimens of polyphenylsiloxane after heating 24 hours at 450°C, still retain up to 3.7% C and 0.67% H, and even after heating 6 hours at 550°C, they still contain 0.33% C and 0.27% H.

The introduction of halogens (chlorine and fluorine) into the phenyl group has no substantial influence on the resistance of the polymers to thermal oxidative degradation, as will be clear from Fig.62, 63, 64, and 65.

The analytical data show that polychlorophenylsiloxane after heating 16 hours at 350°C contains 30.29% Cl and 35.83% C against 36.61% C and 3.20% Cl in the original specimen (Table 100). Consequently, at 350°C the polychlorophenylsiloxanes are degraded very slowly, even without marked cleavage of the chlorine from the phenyl group.

A calculation of the degree of degradation of polyorganosiloxanes may be made starting out from the fact that the losses in the weight of a unit of the polymer chain, for instance, for polymethylsiloxane, CH₃SiO₁.₅, is made up of the weight of the methyl group detached (-15), after subtracting the weight of the oxygen that
Fig. 60 - Degree of Degradation (in Percentage Loss of Weight) of Polyvinylsiloxane, Related to the Temperature and Duration of Heating

a) Time, hours; b) Loss in weight, %

Fig. 61 - Degree of Degradation (in Percentage Loss of Weight) of Polyphenylsiloxanes, Related to the Temperature and Duration of Heating

a) Time, hours; b) Loss in weight, %

Fig. 62 - Degree of Degradation (in Percentage Loss of Weight) of Polychlorophenylsiloxane, Related to the Temperature and Duration of Heating

a) Time, hours; b) Loss in weight, %

Fig. 63 - Degree of Degradation (in Percentage Loss of Weight) of Polydichlorophenylsiloxane, Related to the Temperature and Duration of Heating

a) Loss in weight, %

Fig. 64 - Degree of Degradation (in Percentage Loss of Weight) of Polychlorophenylsiloxane, Related to the Temperature and Duration of Heating

a) Time, hours; b) Loss in weight, %
adds instead of two methyl groups, which amounts to 10.45% of the weight of the structural unit. It is easy to see that during the "time of half disintegration" (C/Si = 0.5)*, the loss in weight amounts to half of 10.45 (5.22%).

At a temperature of 350°C, the time of half disintegration (cf. Table 99) is about 2 hours; in this case the C/Si ratio amounts to 0.47, and the weight loss to 6.02%, which is close to the calculated quantity (5.22%).

By using the degradation curves, the "time of half disintegration" of the polymers at various temperatures was determined (Table 101).

These data show that polyorganosiloxanes with a three-dimensional molecular structure are more resistant to thermal degradation than those with a linear structure.

Fig. 65 - Degree of Degradation (in Percentage Loss of Weight) of Polychlorophenylsiloxane, Related to the Temperature and Duration of Heating
a) Time, hours; b) Loss in weight, %

### Table 100

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Conditions of Degradation</th>
<th>Weight Loss %</th>
<th>Elemental Composition %</th>
<th>Converted to Weight of SiO₂ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C₆H₄SiO₃]₉₆</td>
<td>24 hrs at 450°</td>
<td>52.0</td>
<td>C: 0.67, H: 0.33, Si: 0.33</td>
<td>91.74</td>
</tr>
<tr>
<td></td>
<td>6 hrs at 550°</td>
<td>57.5</td>
<td></td>
<td>96.28</td>
</tr>
<tr>
<td>[C₆Cl₄SiO₃]₉₆</td>
<td>6 hrs at 450°</td>
<td>57.0</td>
<td>C: 0.21, H: 0.13, Si: 1.45</td>
<td>97.70</td>
</tr>
<tr>
<td></td>
<td>10 hrs at 350°</td>
<td>6.4</td>
<td></td>
<td>97.67</td>
</tr>
<tr>
<td>[Cl₆C₆H₄SiO₃]₉₆</td>
<td>6 hrs at 550°</td>
<td>70.0</td>
<td>C: 0.63</td>
<td>45.16</td>
</tr>
<tr>
<td></td>
<td>6 hrs at 550°</td>
<td>72.5</td>
<td>H: 0.82</td>
<td>45.77</td>
</tr>
</tbody>
</table>

*"The time of half-disintegration" is the time necessary for the oxidative rupture of half of all the C-Si bonds of the polymer; in this time the C/Si ratio in the polymer will become equal to 0.5, instead of 1 as in the initial poly-methylsiloxane.
structure may be arranged in the following decreasing order of thermal stability, depending on the composition of their organic radical:

\[ C_6H_5 > ClC_6H_4 > Cl_2C_4H_2 > Cl_3C_3H_2 > CH_2 = CH > CH_2 > C_2H_5 \]

Table 101

Time of Half Disintegration of Polyorganosiloxanes Under Thermal Degradations

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Degradation Temperature °C</th>
<th>Time of half disintegration, hr</th>
<th>Polymers</th>
<th>Degradation Temperature °C</th>
<th>Time of half disintegration, hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>( [CH_3SiO]_n )</td>
<td>250</td>
<td>&gt;24</td>
<td>( [C_6H_5SiO]_n )</td>
<td>350</td>
<td>&gt;24</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>2.0</td>
<td></td>
<td>450</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>0.8</td>
<td></td>
<td>550</td>
<td>0.8</td>
</tr>
<tr>
<td>( [C_2H_4SiO]_n )</td>
<td>250</td>
<td>0.8</td>
<td></td>
<td>( [ClC_6H_4SiO]_n )</td>
<td>450</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>0.7</td>
<td></td>
<td>550</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>0.5</td>
<td></td>
<td>( [Cl_2C_4H_2SiO]_n )</td>
<td>450</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>550</td>
<td>0.7</td>
</tr>
<tr>
<td>( [CH_3CH=CHSiO]_n )</td>
<td>250</td>
<td>&gt;24</td>
<td>( [Cl_3C_3H_2SiO]_n )</td>
<td>450</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>6.5</td>
<td></td>
<td>550</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>550</td>
<td>0.5</td>
<td></td>
<td>( [PC_6H_5SiO]_n )</td>
<td>450</td>
</tr>
</tbody>
</table>

The high stability of a polymer with the vinyl radical is explained by the complexity of the polymeric molecules, in which, owing to the steric effect, the attack of the oxygen on the carbon attached to the silicon atom is hindered.

An analysis of the volatile products formed during the process of thermal oxidative degradation of polymethylsiloxane showed them to consist mainly of carbon monoxide, (25.0%), and water, (17%); there are also small amounts of carbon dioxide, (2%), formaldehyde, (3.7%), and methanol, as well as traces of formic acid (figured on the weighed sample, (cf. pages 814 and 815).

A consideration of the experimental data obtained allows us to propose the following mechanism for the thermal oxidative degradation of polyorganosiloxanes.

The oxygen of the air attacks the carbon atom attached to the silicon in the polymer molecule; in this case, hydroperoxides are formed at first, and are then
rapidly broken down:

\[
\text{O}_2 \rightarrow \cdot \text{O} - \text{O}
\]

\[
\text{CH}_3 + \cdot \text{O} - \text{O} \rightarrow \text{CH}_2\text{OH}
\]

(I)

The hydroperoxide is cleaved, forming formaldehyde and an OH radical:

\[
\text{CH}_2\text{OOH} + \cdot \text{O} - \text{O} \rightarrow \cdot \text{O} - \text{O} + \text{CH}_2\text{O} + \cdot \text{OH}
\]

(II)

The OH radical reacts with a positively charged silicon atom in the polymer molecule by adding to it:

\[
\cdot \text{O} - \text{Si} - \text{O} + \cdot \text{OH} \rightarrow \cdot \text{O} - \text{Si} - \text{O}
\]

(III)

\[
\cdot \text{O} - \text{Si} - \text{O} + \cdot \text{OH} \rightarrow \cdot \text{O} - \text{Si} - \text{O} + \text{H}_2\text{O}
\]

(IV)

The formaldehyde, on thermal cleavage forms mainly carbon monoxide and hydrogen

(Bibl. 96)

\[
\text{CH}_2\text{O} \rightarrow \text{CO} + \text{H}_2
\]

(V)

For this reason carbon monoxide is the principal gaseous product of degradation.

F-TS-9191/V 869
Part of the formaldehyde, under the conditions of our experiments, is oxidized to carbon dioxide

\[ \text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]  

(VI)

and to formic acid. The existence of this reaction explains why the quantity of water obtained on the analysis is somewhat greater than could have been liberated by the condensation of the hydroxyl groups formed (Formula IV).

This mechanism is confirmed by the following:

(1) the formation of formaldehyde, CO, and H\textsubscript{2}O on the thermal oxidative degradation of polymethylsiloxanes, and the good agreement between the calculated and found cleavage products;

(2) by the formation, in large quantities, of hydroxyl groups at the temperatures at which an intense disruption of the Si-C bonds in the polymers takes place. In this case, the HO group enters with difficulty into condensation at a high temperature, owing to the fact that the contact between them is hindered.

On conduct of the degradation of polymethylsiloxane in two experiments, the following results were obtained.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Weighed Sample, g</th>
<th>Loss of Weight, g</th>
<th>Water Content, g</th>
<th>Water Content, %</th>
<th>Carbon Monoxide Content, g</th>
<th>Carbon Monoxide Content, %</th>
<th>Carbon Dioxide Content, g</th>
<th>Carbon Dioxide Content, %</th>
<th>Heavy Hydrocarbons Content, g</th>
<th>Heavy Hydrocarbons Content, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1.0676</td>
<td>0.1104</td>
<td>0.1855</td>
<td>17</td>
<td>0.2720</td>
<td>25</td>
<td>0.0219</td>
<td>2</td>
<td>0.0029</td>
<td>0.2</td>
</tr>
<tr>
<td>II</td>
<td>1.0900</td>
<td>0.00678</td>
<td>0.1541</td>
<td>14.1</td>
<td>0.2291</td>
<td>20.9</td>
<td>0.0397</td>
<td>3.6</td>
<td>0.0063</td>
<td>0.6</td>
</tr>
</tbody>
</table>
Analysis of the specimens after degradation gave the following results:

<table>
<thead>
<tr>
<th></th>
<th>Experiment I</th>
<th>Experiment II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Results of analysis, %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>3.97</td>
<td>6.15</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>1.13</td>
<td>1.83</td>
</tr>
<tr>
<td>Silicon</td>
<td>44.52</td>
<td>44.5</td>
</tr>
<tr>
<td>Hydroxyl groups</td>
<td>—</td>
<td>0.48</td>
</tr>
<tr>
<td>Water</td>
<td>—</td>
<td>0.02</td>
</tr>
<tr>
<td>H/C ratio, %</td>
<td>3.42</td>
<td>3.58</td>
</tr>
<tr>
<td>C/Si ratio, %</td>
<td>0.20</td>
<td>0.32</td>
</tr>
</tbody>
</table>

The quantities of CO and H₂O liberated were calculated from these analytical data. Comparison with the quantities found shows the quantity of CO liberated to be close to the calculated value, while the quantity of water liberated exceeds that calculated.

The calculation was based on the following data:

Experiment I. According to the analysis, the C/Si ratio is 0.20; consequently 0.80 mol of CH₃ groups was degraded for each silicon atom. The weighed sample contained 0.0162 mol of CH₃; consequently, 0.01295 mol (or 0.1943 g) of CH₃ was degraded. Hence the calculated quantity of CO should be 0.3622 g.

Found: 0.2720 g CO
  0.0139 g CO (on account of the CO₂)
  0.0340 g CO (on account of CH₂O)
  0.0262 g CO (on account of CH₃OH)

Total: 0.3461 g CO

The quantity of water liberated by the oxidation of 0.1943 g of CH₃, provided the two hydroxyls formed condense to water, should be 0.1166 g. Found: H₂O 0.1855 g.

Experiment II. The weighed sample contained 0.0163 mol of CH₃. The C/Si ratio in the polymer after degradation is 0.32; therefore 0.68 mol of CH₃ groups was degraded (0.011134 mol CH₃ = 0.1670 g CH₃). From this quantity of CH₃, 0.3117 g of CO should be obtained.
Found: 0.2291 g CO

0.0253 g CO (on account of \( \text{CO}_2 \))
0.0340 g CO (on account of \( \text{CH}_2\text{O} \))
0.0262 g CO (on account of \( \text{CH}_3\text{OH} \))

Total: 0.3146 g CO

The quantity of water liberated by the oxidation of 0.1670 g of \( \text{CH}_3 \) should amount to 0.1002 g. Found: \( \text{H}_2\text{O} \) 0.1541 g.

This mechanism of reaction allows us to predict the thermal stability of the polyorganosiloxanes from the structure of the organic radical or groups attached to the silicon atom.

Thus, according to the degradation mechanism which has been presented above, it is easy to understand why polyethyilsiloxane is degraded more readily than polymethylsiloxane: the point is that the \(-\text{CH}_2-\) group of the ethyl radical attached to the silicon atom is more easily oxidised than the \( \text{CH}_3- \) group.

It should be noted that the polyorganosiloxanes with linear chains are more sensitive to thermal oxidative degradation than the polyorganosiloxanes, which consist of cross-linked and three-dimensional molecules. It is very clear here how an insignificant quantitative modification in the chemical composition of the polymer, leading to a qualitative modification in its structure, allows us to prepare high-molecular substances of sharply different properties. This is explained by the fact that a change in the molecular structure from linear to three-dimensional leads to a considerable restriction of the mobility of the molecules at high temperatures. In polymers with linear molecules, the mobility of the chains is restricted by the rigidity of the single Si - O bond. The disruption of such a molecular chain involves the rupture of a single Si - O bond. In polyorganosiloxanes, thermal oxidative degradation may proceed either at the less energetically stable Si - C bond or at the stable bond Si - O. To rupture the Si - O bond, a more energetic barrier must be overcome than to rupture the Si-C bond, but here the structure of the linear mol-
ecules in the polyorganodisiloxanes must be taken into account. Recent data indicate that the molecular chains in polydimethylsiloxanes are of spiral structure, with three or more silicon atoms in the spiral (Bibl.94). When the polymer is heated to high temperatures, such a structure creates favorable conditions for rupture of the chains and ring-closure. This view is also confirmed by experimental observations. When polydimethylsiloxane is heated in vacuo to high temperatures, it breaks down into low-molecular cyclic polymers without appreciable rupture of the Si-C bonds.

\[ [R_xSiO_y] \rightarrow (R_xSiO)_n + (R_xSiO)_m + (R_xSiO)_n. \]

On degradation in vacuo, the spiral structure of the molecular chains exert a greater influence on the process than the difference between the Si-C and Si-O bond energies.

Under thermal oxidative degradation of polydimethylsiloxane and polydiethylsiloxane, destruction of the molecules is observed not only at the Si-C bond, but also at the Si-O bond.

The rupture of the Si-O bond is already observed at 300°C, and at 400°C it proceeds at great intensity. After 3 hours of heating, one specimen of polydimethylsiloxane lost 60% of its weight.

In polyorganosiloxanes with a three-dimensional molecular structure (including cyclic polymers as well):
the detachment of a unit of the chain, or of a large segment of the chain of the
polymeric molecule involves the necessity of its rupture at three "points", or at
two, if the polymer contains cross-linked molecules. This, in turn, involves the
destruction of two or three energetically stable Si-O bonds. For this reason no
destruction of the molecular chains at the Si-O bond is observed in polyorganosilox-
anes with a three-dimensional structure, regardless of the nature of the organic
radical, even at 550°C.

Cementing and Impregnating Compositions and Materials Based on Organosilicon
Compounds

The hydrolyzed esters of orthosilicic acid are most widely used as cementing
and impregnating compositions. They are able to cement various inorganic materials,
and have found application in the manufacture of cement, making molds for precision
casting, the impregnation of various porous materials, etc.

Cements

Cements are prepared by mixing a hydrolyzed ester of orthosilicic acid with a
filler.

Aluminosilicate, sillimanite, quartz flour, talc, slag, and pigments may be
used as the filler. One of the most essential factors determining the strength of
the composition is the grain-size composition of the filler, which is so chosen that
the interstices between the large particles shall be filled at maximum density with
small particles (2 - 5 μ).

Better results are obtained when the binder used is a partially hydrolyzed es-
ter containing 1.5 - 2% of a condensing agent. Before the article is molded, tech-
nical (97%) ethyl alcohol is added to the mixture of ester and filler. The optimum
quantity of moisture necessary for completion of the hydrolysis ranges from 3 to 5%
of the quantity of ester. If more than 6% of water is introduced, the number of
residual ethoxy groups will be diminished, so that the strength of the article suf-
fers appreciably, and it can be extracted from the mold only with difficulty. If, on the other hand, the quantity of water drops to 1.8%, then the drying time lengthens to several weeks, but the strength of the cement doubles, provided the drying is in air. We give a few recipes for cement compositions:

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filler, g</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Hydrolyzed ester with 2% of condensing agent, mg</td>
<td>14</td>
<td>18</td>
<td>12</td>
</tr>
<tr>
<td>Technical ethyl alcohol (94%), ml</td>
<td>7</td>
<td>6</td>
<td>6</td>
</tr>
</tbody>
</table>

After the mixture has been mixed, it is loaded into the mold and subjected to vibration for a few minutes, after which it is hardened in air or in a kiln. The following data characterize the increase in the strength of an article (Recipe I) when heated gradually:

<table>
<thead>
<tr>
<th>Strength of article, kg/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>After 24-hour air drying</td>
</tr>
<tr>
<td>After sintering at 300°C</td>
</tr>
<tr>
<td>at 700°C</td>
</tr>
<tr>
<td>at 1000°C</td>
</tr>
<tr>
<td>at 1500°C</td>
</tr>
</tbody>
</table>

Thus there is a considerable gain in strength at a temperature over 1000°C. An article made by Recipe I has an absolutely smooth surface; an article made by Recipe II has a surface recalling that of porcelain. Recipe III gives a composition with minimum shrinkage, allowing precise reproduction of the assigned measurements of an article.

Cement hardened in the cold is resistant to acids and weak alkalies. Water only improves its mechanical properties. The porosity of such an article, determined by immersion in water for 24 hours, is 0.5%. When sintered at 300°C, the article acquires resistance to concentrated alkali solutions. But sintering also gradually increases the porosity of the article; after heating to 1000°C, its porosity
reaches 11-12%. The porosity may be decreased by treatment with a 5% alcoholic solution of hydrolyzed ester. This leads to filling of the pores, but when the baking is repeated, it results in additional increase of porosity.

A thin layer of cement may be evenly distributed on the inner surface of a steel pipe by rapidly rotating it. The coating has good adhesion to steel and does not crack disintegrate on sintering, in spite of the difference in the coefficients of expansion.

The following temperature conditions may be recommended for sintering cement mixtures:

<table>
<thead>
<tr>
<th>Process</th>
<th>Temperature</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air drying</td>
<td></td>
<td>24 hours</td>
</tr>
<tr>
<td>Heating</td>
<td>to 100°C</td>
<td>2 hours</td>
</tr>
<tr>
<td></td>
<td>to 100°C</td>
<td>1 hour</td>
</tr>
<tr>
<td></td>
<td>to 200°C</td>
<td>2 hours</td>
</tr>
<tr>
<td></td>
<td>to 500°C</td>
<td>2 hours</td>
</tr>
</tbody>
</table>

The temperature may then be increased at any rate desired. In this way articles resembling ceramics can be manufactured on the base of hydrolyzed tetraethoxysilane, using either kiln or air drying, and the metal parts can be inserted in them without any risk of corrosion. The adhesion of the cements may be strengthened by adding a solution of vinyl acetate in a mixture of alcohol and acetone to the alcohol used for the hydrolysis. The porosity and moisture adsorption may be reduced to a minimum by adding alkylpolysiloxanes to the composition.

Hydrolyzed tetraethoxysilane may be used as a binder for abrasive wheels. The mixture of abrasive powder with hydrolyzed tetraethoxysilane, after molding, is dried and fired as with the cement compositions.

**Precision Casting (Dibl.24)**

The use of hydrolyzed tetraethoxysilane in making molds for what is termed precision casting is of very great importance. By means of such molds, castings can
be made to reproduce the assigned dimensions within 0.2 mm, and very vital parts can be produced with relative ease. There is a very extensive literature devoted to the use of tetraethoxysilane in mold-making for precision casting. We present one of the methods of making molds and castings, the wax pattern method.

Mold-making for precision casting. A wax pattern of the article is made in a mold of fusible alloy (for instance, of bismuth and tin). A set of wax patterns is sprinkled (with an atomizer) with a mixture of partially hydrolyzed ester and a condensing agent (2%), alcohol, water, and a finely ground filler that resists the metal being cast, at its melting point (aluminosilicate or quartz flour). After the wax patterns have been dried in air, they are coated with a second layer, again dried, and molded with a mixture of hydrolyzed ester, alcohol, water and filler, which contains, together with fine granules, also coarse particles, for instance floor sand. The mold is placed on the vibrating table, and then air-dried for 2½ hours. The wax is then melted out at low heat, and the mold is then gradually heated to 800-1000°C. After the mold has cooled, the metal is poured into it. It is then cooled and knocked out. The article is removed from it and sand-blasted. Sometimes hydrolyzed sodium silicate is used instead of tetraethoxysilane to spray the wax patterns. In this case, the presence of sodium ions lowers the melting of the metal being cast. Without a condensing agent, sodium silicate gives more reliable results than tetraethoxysilane, but in the presence of a condensing agent it is simpler and better to work with tetraethoxysilane.

Impregnating Compositions

Hydrolyzed tetraethoxysilane is also used to reduce the porosity of various materials. An impregnating mixture is prepared by mixing 315 liters of tetraethoxysilane with a mixture of 50.7 liters of water and 135 liters of technical 94% alcohol until dissolved, after which 250 liters more of tetraethoxysilane is added to the mixture. Impregnation with it can increase the resistance to water of such materials as bricks, graphite, asbestos, paper, leather, cork, textiles, or stucco.
Highly porous materials are impregnated and dried twice (Bibl.33). To preserve wood from rotting, it is impregnated with phenol or naphthol esters of orthosilicic acid, hydrolysed in the presence of ammonia or alkaline salts.

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